STUDIES IN ADSORPTION BY TEXTILE FIBRES

BY

ARUNKUMAR HARILAL TOLIA

A Thesis submitted to the University of Glasgow in fulfilment of the regulations governing the award of the Degree of Doctor of Philosophy in the Faculty of Science.

Colour Chemistry Research Laboratory,

Department of Chemical Technology,

Royal College of Science and Technology,

Glasgow.

August 1963.

CONTENTS

Acknowledgements

The author wishes to express his gratitude and sincere thanks to Dr.C.H.Giles for his encouragement and guidance throughout the present investigation and to Professor P.D.Ritchie, F.R.S.E., for the interest he has shown in this work.

Thanks are also due to Professor R.Meredith, F.R.S.E., and to Dr.N.Peacock for some valuable discussions and to Dr.D.Smith for the statistical analysis of some of the results.

Publications

The work described in this thesis has been included in the following papers.

In Print:

Part II

"Studies in Adsorption. Part XV. Some Aspects of the Kinetics of Dyeing Gelatin and Wool", by C. H. Giles, A. P. Montgomery and A. H. Tolia, Textile Res. J., 1962, 32, 99.

In Preparation:

Part I

"Adsorption of Organic Vapours on Wool", by H. M. Elder, C. H. Giles and A. H. Tolia.

Part III

"Measurement of External Surface Area of Fibres", by C. H. Giles and A. H. Tolia.

A paper is also in preparation dealing with the statistical analysis of the relation between fastness data and structure of dye molecules, which includes a part of the work described in Part II of this thesis.

SUMMARY

This thesis describes a series of investigations designed to apply the available fundamental knowledge of the adsorption process to the understanding of some of the problems concerned with the surface characteristics of textile fibres, and its effect on adsorption process.

Part I of the thesis is concerned with investigations to study the effect of the size of adsorbate molecule on the rate of adsorption on wool fibres and the influence of pores of varying sizes in the wool. The physical state of dye in air-dry wool fibres has also been investigated. The vapour phase adsorption technique has been followed and it is shown that vapours with similar active groups but different molecular size show a considerably slower rate of adsorption on wool fibres with increase in adsorbate molecule size, the saturation adsorption decreasing at the same time. This has been attributed to the presence of pores on the wool surface, the size and distribution of these pores determining both the rate of adsorption and the saturation adsorption. An attempt has been made to calculate the pore-size distribution in wool fibres. The similar experiments on dyed wool fibres indicate a lower rate of adsorption for these vapours and also a lower saturation adsorption. Since the rate and the saturation adsorption are not very much lower at high concentration of dye in fibres, it is suggested that the process is affected by the blocking of /...

of pores by dye aggregates rather than the inactivation of similar adsorption sites for dyes and vapours.

Part II is concerned with the study of relative rates of adsorption by wool and gelatin for a number of series of sulphonated azo acid dyes and 2:1 dye-metal complexes. It is shown that: (i) The rate of adsorption of each dye by a given area of the external surface of gelatin is about four times that by the same area of the external surface of wool; (ii) the logarithm of the rates falls linearly with both the number of substituent groups in the dye molecule and with its molecular volume; each series of dyes giving points lying on a different line.

A statistical study of wash fastness and migration property data for a number of acid dyes shows that these properties are significantly dependent on the total number of atoms or the number of carbon atoms alone, in a dye molecule. Thus wash fastness is shown to increase with increasing size of the dye molecule, while the ease of migration falls.

A few experiments, including measurements of absorption spectra, are described in which benzyl alcohol, and to a less extent dioxan, tends to disaggregate dyes of low basicity when added to their aqueous solutions, but D-glucose and inositol do not do so. Of these solutes, only benzyl alcohol is effective in accelerating dyeing. It is considered that the mechanisms already proposed to account for the acceleration of dyeing by addition of solvents probably all operate, but /...

but the most important may be the effect of adsorption of the solvent by the fibre. On the basis of these results, the very rapid adsorption of benzyl alcohol by wool is attributed to its low molecular volume and non-ionic nature.

Part III is concerned with the development of a new chemical method for the measurement of the external surface areas of textile fibres and the method has also been used on paper pulp fibres. The method is based on the solution adsorption method for measuring surface areas of powders etc., but modification was necessary when applying it to textile fibres because of their porous structure. The adsorption isotherms at short intervals of time are determined, instead of at equilibrium, and the surface areas calculated from these isotherms are extrapolated to zero time. The apparent surface area at zero time has then been assumed to be related to the true external surface area of fibres, and the results compared with those obtained by microscopic and air-permeability methods. A good agreement between the results by different methods has been observed. Chemically modified wool fibres and paper pulp fibres beaten for different intervals of time showed changes in external surface areas reflecting the changes in the fibre surface with different treatments. External surface areas are found to vary with different non-polar solvents when p-nitrophenol is the solute, and this has been related to the solubility of the solute in different solvents. Use of non-polar solvents in which p-nitrophenol is sparingly soluble is recommended.

GENERAL INTRODUCTION

The aim of the present investigations was to apply existing knowledge of adsorption mechanisms to several systems which have not previously received much attention. The work covers mainly three topics, (i) study of the rate of adsorption of different vapours on wool treated in different ways, (ii) study of the kinetics of dyeing of wool fibres and gelatin, with a series of dyes specially selected for their chemical and physical structures and (iii) measurements of external surface areas of fibres by adsorption methods. These are described in Parts I, II, and III of this thesis respectively. Most of the work in the present thesis is confined to adsorption at solid-liquid interfaces, but some concerns adsorption at solid-vapour interfaces.

Adsorption[1,2,3,4]

As early as the eighteenth century, Scheele and Fontana independently observed that charcoal combines with gases and vapours with a reduction in total volume, and Lowitz removed coloured materials from solution with the same solid. Although similar observations were made from time to time of this tendency to the accumulation of one phase at the interface with another, very little was known concerning the nature of the process.

Since then the subject has been studied in very great detail by a number of workers, and it is now known that the surface of a liquid is in a state of strain, or unsaturation, and that of a solid has, similarly, a /...

a residual field of force; there will consequently be a tendency for the free energy of any surface to decrease, and it is this tendency which is ultimately responsible for the phenomenon of adsorption. The term adsorption refers strictly to the existance of a higher concentration of any particular component at the surface of a liquid or of a solid phase than it is present in the bulk. The phase which accumulates other phases on its surface is called the "adsorbent" and the component which becomes preferentially adsorbed on the surface of the adsorbent is called the "adsorbate". Adsorption is usually a reversible process, and under the given conditions, when the number of adsorbate particles becoming attached to the adsorbent is equal to the number leaving it, the equilibrium is said to have been established.

Forces Acting in Adsorption

The exhaustive research done on adsorption in recent years has revealed that in most systems more than one force is responsible for the adsorption mechanism, and the predominent force will depend on the type of the system. The principal types of forces are: van der Waals attraction forces (physical), hydrogen bonding, covalent bonding and ion exchange.

Van der Waals Forces: These are essentially short-range physical forces and include such forces as orientation forces (attraction between permanent dipoles), induction forces (attraction between permanent dipoles and induced dipoles), attraction between ions and dipoles and dispersion forces (quantum-mechanical interaction between momentary dipoles). /...

dipoles). The important feature of these forces is that when they are operative no chemical bonds are made or broken and hence the chemical nature of the adsorbate remains unchanged.

An important example of the action of these forces is found in the dyeing of wool and nylon with acid dyes. Here the inorganic anions are first attached to the active sites in the fibre which are then replaced by the dye anions which are much larger than the inorganic anions. This replacement must be largely due to the van der Waals mutual attraction between the aromatic nuclei of the dye and that between these and the hydrophobic parts of the protein chain molecules[4]. It has also been shown[5] that dry wool and nylon under certain conditions can adsorb certain aromatic compounds, e.g. benzene and stilbene, from dry solvents, and this has been attributed mainly due to the van der Waals forces.

Hydrogen Bonding: This may occur by either (i) hydrogen donation or (ii) hydrogen acceptance, by the solute.

Many instances of type (i) have been discovered, e.g., silica is believed to adsorb phenols, amines etc. from aqueous and non-aqueous solvents in this way, the hydrogen atoms being donated by the solute to the surface oxygen atoms[6].

Process (ii) is believed to occur with hydrogen acceptor solutes, e.g., nitrobenzene, azobenzene, etc., when they are adsorbed by alumina. There is also evidence to suggest that ethanol is bonded to free hydroxyl groups in the alumina surface[7], and the ethanol is believed to /...

to be acting as an hydrogen acceptor.

Covalent Bonding: This process, often called "chemisorption" appears to be rather uncommon. Adsorbed molecules when covalently bonded to the adsorbent, are usually extremely difficult to remove. It is encountered in some forms of textile dyeing, e.g., reactive dyes on cellulose and nylon[8], where a covalent bond is formed between the triazinyl or other "reactive" nucleus and hydroxyl groups in the substrate; and perhaps in the dyeing of anodised aluminium with mordant dyes[9]. Work at present in progress in this laboratory however appears to throw doubt on the role of chemisorption in the last mentioned case[10].

Ion Exchange: This may be regarded as a redistribution of ions between one environment and another. The ions keep their charges when adsorbed and no covalent bonds are made or broken. In many cases ion exchange is characterised by a rapid attainment of equilibrium.

An example is found in adsorption of cations by silica from aqueous solution[6], and of cations by technical alumina[11] (which is alkaline in reaction owing to the presence of some sodium carbonate impurity).

Factors Affecting the Adsorption Mechanism

Adsorption is indeed a very complex process and there are many factors arising both from the nature of the adsorbent and the adsorbate, and also some external factors, which influence the process. A complete account of these cannot be given, because of the vast volume of /...

of available data and because of the many unknown factors involved. However, the more important and commonly predominant factors are summarised below.

Physical Properties of the Adsorbent: The solids are divided into two classes, crystalline and amorphous. The crystalline solids have a well defined structure with constituent particles arranged in a regular fashion and they have reproducible properties, e.g., sharp melting points. The amorphous solids have a random structure, and do not possess a sharp melting point.

In the case of crystalline surfaces with faces, corners and edges in large numbers, it has been found[12] that molecules in different locations have different energies. Thus at the corners of the crystal the molecules are most exposed, and so are most reactive, consequently higher adsorption occurs. In general, in crystalline surfaces the disposal of sites at which adsorption can occur will be in a regular pattern and hence the adsorption may have some stoichiometric relation to the number of available sites.

If the surface of the solid contains capillaries and fissures, then the adsorption of small particles which can enter the capillaries will be favoured, while the larger molecules may enter slowly or may not be able to enter at all. This "molecular sieve" effect has been investigated by the author in the study of adsorption of different vapours on wool (see Part I).

The presence of impurities on the surface of the adsorbent markedly changes its chemical properties, and consequently its adsorption /...

tion properties. It is often difficult to tell whether a given effect is due to impurities or to some other physical circumstances, but a trace of water in the adsorbent has been found, by many workers, to alter the adsorption properties.

Properties of the Interface: Adsorption is a process where the adsorbed molecule is confined to a surface and hence certain some degree of freedom is lost; this is accompanied by a decrease in free energy, $-\Delta G$. This decrease is a measure of the affinity of adsorption, which in the case of a solid-liquid phase or in binary liquids, or in the case of a solvent with more than one solute, is also affected by other factors; these include competition between the components in the system, the nature of the active sites on the adsorbent and the size and shape of the adsorbate molecules. In the case of solvents containing more than one solute competition depends on the dimensions of the solute molecules and their affinity for the adsorbent. Thus a large particle with more than one active group may occupy several sites, which might otherwise have been taken by small particles, or they may only block these sites without actually occupying them. In contrast, particles with several active groups distributed along the periphery may be adsorbed in lower quantities than those with active groups at one end only, for the latter may be adsorbed with an end-on orientation and thereby cover less area than the former lying flat.

Examples of competition between different solvents have been studied by Kipling[7], who used binary mixtures of miscible liquids, and found /...

found that from a mixture of ethanol and benzene, ethanol is preferentially adsorbed by α-alumina, but benzene is preferentially adsorbed by charcoal.

Interaction between the Component Particles of the Liquid Phase: Various types of interaction forces acting between the components of the liquid phase also affect the process of adsorption. Thus the solvation forces between the solute and the solvent tend to exert a "viscous drag" on the solute which consequently tends to retard adsorption. Thus solutes with high solubility in the solvent are adsorbed to a lesser degree than solutes with low solubility. This phenomenon was observed in the present work (see Part III) when surface area measurements on fibres were carried out. Here the solute, p-nitrophenol (PNP), was adsorbed for different lengths of time on fibres, from different solvents, and it was found that the solvents in which PNP is highly soluble tend to retard adsorption as compared with other solvents in which PNP is scarcely soluble. This is discussed later in this thesis.

Temperature: Adsorption is essentially a process accompanied by the evolution of heat, and it would be expected to be favoured by low temperatures. This is true for most cases, where adsorption is found to be greater the lower the temperature. If the heat of adsorption is low, this difference is less marked. A few anomalous cases have been reported[13] where adsorption (in water) is lower the lower the temperature. This has been attributed to the high degree of aggregation of the solute molecules in dilute aqueous solutions, because the effect of temperature /...

temperature is normal when a disaggregating solvent is used.

The Adsorption Isotherm

The results of equilibrium adsorption measurements are usually expressed in the form of an "adsorption isotherm". In the solid-liquid systems the change in the concentration of a solute adsorbed on the adsorbent with change in the concentration of the solute in the solvent is followed, at a fixed temperature, while in solid-vapour systems the adsorption isotherm is usually obtained by plotting the change in vapour pressure against the change in the volume of vapour adsorbed.

A large number of different types of isotherms have been reported in the literature, and some workers have classified them by shape. Thus Brunauer[14] has classified all vapour phase adsorption isotherms in five types, called Types I-V.

Recently Giles and coworkers[15,16] have proposed a system for classifying solution adsorption isotherms. All the isotherms are divided into four main classes according to their initial slope, and each class is then divided into sub-groups depending upon the shape of the upper part of the isotherm. The four classes are S, L (i.e., Langmuir type), H (high affinity) and C (constant partition) isotherms.

The S Isotherm: This isotherm is obtained in systems where the solute molecule has a fairly large hydrophobic residue with a marked localisation of attractive forces over a short section of its periphery, has moderate interaction with other solute particles and meets with strong competition with the solvent. The adsorbed particles are believed /...

believed to be oriented vertically to the plane of the interface and are stacked face-to-face.

The L Isotherm: This is the most common form; the solute molecules are believed to be oriented flatwise on the adsorbent, or adsorbed as micelles.

The H Isotherm: This is regarded as a special case of the L isotherm in which the solute has a very high affinity for the adsorbent, so that it is completely withdrawn from dilute solutions, and the initial part of the isotherm is therefore coincident with the vertical axis. The H isotherm is often obtained when the solute is adsorbed as large units (e.g., micelles) but it is not uncommon with single ions particularly if adsorption is mainly due to ion-exchange.

The C Isotherm: This is characterised by the constant partition of solute between solution and substrate, right up to the maximum adsorption, where an abrupt change to a horizontal plateau occurs. The C isotherm is usually obtained when the substrate is mainly porous with regions of differing degrees of crystallinity, as in the case of many natural fibres, and when the solute has a much higher affinity for the adsorbent than the solvent has.

Adsorption and Surface Area

In solid-vapour phase systems, the adsorption isotherm has been widely used to estimate the surface area of the solid. The principle of the method is to determine the amount of adsorbate required to form a monolayer on the adsorbent surface; from the adsorption isotherm, and /...

and from the size of the molecule and its probable orientation on the surface of the adsorbent, to calculate the surface area covered. In solid-liquid phase systems also a similar method is followed. The most widely used adsorbates in this case are different types of dyes, mainly because they are easy to analyse, by colorimetric means. However, the main disadvantage in using dyes for surface area measurements is that they tend to aggregate in aqueous solutions and consequently present some problems in calculation. The molecular size is also slightly difficult to determine in some cases. Recently p-nitrophenol has been found to be very satisfactory by Giles et al.[17], because it is a comparatively simple molecule and hence its size is known with fair accuracy, and it is strongly adsorbed by a variety of solids.

Orientation

In surface area measurements by adsorption methods, the orientation of the adsorbate molecule on the surface plays a very important part. The calculations of surface area are of course dependent on the mode of orientation of the adsorbed molecules. In a given system, the thermal motion will tend to orient the adsorbed molecules randomly, whereas the forces responsible for adsorption as well as the effects of neighbouring adsorbed molecules will tend to give them a preferred position.

The mode of orientation of the adsorbed molecule is usually dependent on the types of reactive groups it has and its disposition on /...

on the molecule, and as stated before it is usually reflected in the type of isotherm it gives.

Coverage

Coverage is a measure of the proportion of the surface occupied by the adsorbate molecule to the bare surface. Thus the situation on the surface will depend greatly on the amount adsorbed. When the amount adsorbed is very low, we deal essentially with a bare surface of adsorbent on which a few adsorbate molecules are present, far away from each other. With increasing adsorption the surface becomes more and more covered with the adsorbate molecules and the situation arises when they form a complete single layer, and they may then build up subsequent layers to form a "multilayer" system.

One important assumption in measuring surface areas by this method is that the adsorbate molecules form a compact monolayer on the adsorbent surface. Recently the author's colleagues[18] have shown that there is in many cases a relationship between the molecular weight of a dye and the extent to which it is adsorbed in excess of a monolayer.

Present Work

Work was started to follow up the experiments by Elder et al.[19] who have shown that in the case of wool dyed with different types of dyes, e.g., levelling, or milling acid dyes, the rate of uptake of ethyl alcohol vapour changed very markedly with the nature of the dye. This seemed to demonstrate physical blocking of pores in the fibre by the dyes. The results of the author's work are presented in Part I of the thesis; they demonstrate a molecular sieve action by wool fibres towards vapours of different molecular weight.

The study of the sieve action by wool fibres was extended to solution adsorption, and the rate of dyeing of different dyes on wool and gelatin has been examined; the results are given in Part II. It is apparent that there is a direct relation between rate of adsorption and the volume of the dye molecule.

By using a solvent with molecules too large to penetrate readily between the fibre molecules in absence of water it is possible to measure external surface area of fibres by solution adsorption with a strongly-bonding solute of small molecular size, e.g., p-nitrophenol. The solvent should enter the fibre only very slowly if at all and so permit rapid adsorption on the external surface only. It was also decided to investigate whether dyes in water could be used in place of p-nitrophenol for these surface area measurements. A basic dye (Rhodamine B) was used; this had already been used in this laboratory in adsorption tests on various substrates and its mode of orientation on various surfaces had been worked out[20]. The results of these investigations are presented in Part III.

PART I

ADSORPTION OF ORGANIC VAPOURS ON WOOL

Introduction

The study of adsorption of organic vapours on textile fibres has not received much attention, though adsorption from aqueous solution has been studied extensively. This is difficult to understand as such study can be of importance in understanding the internal structure of fibres as well as their behaviour towards dyeing and finishing chemicals.

Almost all the important fibres have been studied with respect to water vapour adsorption, probably because the mechanical properties of fibres are greatly influenced by humidity conditions; and also a clear understanding of the mode of attachment of water molecule can be of great help in understanding many adsorption phenomena and the internal structure of fibres. Thus Sheppard and Newsome[21] made the first suggestion that the hydroxy groups in cellulose are responsible for attracting water molecules during adsorption. Bull[22] made an extensive study of water vapour adsorption on protein fibres and nylon and found that it followed Brunauer's isotherm. He calculated the B.E.T. constants and the surface areas from the water isotherms and also the free energy changes accompanying adsorption. He believes that his results corroborate the view that protein molecules in the solid state are linked together to form coherent planes whose exposed surfaces are hydrophilic, water being adsorbed between these planes. Hailwood and Horrobin[23] assume water to be present in three phases in the fibre, viz., dissolved water, unhydrated water /...

water molecules and hydrated water molecules, all forming an ideal solid solution; they found experimental evidence to support their mathematically-treated hypothesis.

According to Speakman[24], the adsorption-desorption isotherms of water vapours on different varieties of wool show that their adsorptive capacities are very similar and that differences between varieties appear to be related to their relative fineness. From a study of the treatment of wool with formaldehyde and with nitrous acid, both of which react with the amino groups of the fibre, he also concluded that these groups play a relatively insignificant part in water adsorption by untreated wool, since wool treated in this manner was only slightly less hygroscopic than the corresponding untreated material. The latter statement is, however, contradictory to the observations of Trotman[25] who has shown that wool treated with formaldehyde loses 30% of its original affinity for water.

Larose[26] in his experiments on the adsorption of water vapours on wool dyed with Orange II observed a reduction in adsorption of water vapour on dyed wool, which was roughly proportional to the amount of dye present. This was interpreted by him as evidence of water and dye being adsorbed on the same sites, viz., the side chain amino-groups.

The adsorption of water vapour by proteins and other polymers seems to give rise to three types of isotherms[27], corresponding to solution adsorption; van der Waals adsorption and capillary condensation /...

condensation or multilayer adsorption. Though the researches on the adsorption of water vapours on textile fibres has led to much speculation (e.g., see the two reviews[27,28]), it is appreciated that no single theoretical approach adequately covers the problem of how water is held by polymers over the entire relative vapour pressure range, and the different theories are criticised by different workers. Thus the isotherms of Pierce[29] and Cassie[30] have been criticised by Gilbert[31].

Of the little information available on the adsorption of vapours of organic compounds on textile fibres the work of Kanamaru and Chao[32] and Lauter[33] may be mentioned. They adsorbed a number of simple organic compounds, principally alcohols on cellulose and its derivatives, and showed that the sigmoid shape of the isotherms of hydroxy compounds is related to the fibre swelling.

King[34] adsorbed vapours of water, methanol, ethanol and n-propanol on wool and observed a sudden rise in the temperature of the fibre when vapour was first introduced, but the temperature then slowly returned to its initial level. This rise is caused by the evolution of heat in the reaction between the fibre and the adsorbate, and it was shown to have a significant effect in retarding the initial diffusion by reducing the adsorption of the vapour at first. The temperature rise was greatest with water and least with ethanol, because the slower the rate of diffusion of the adsorbate molecule into the fibre, the more readily can the heat of adsorption be dissipated.

Chipalkatti et al.[35] in their study on adsorption of a number of organic /...

organic compounds in vapour form on wool and nylon, observed that all hydroxylic compounds showed considerably greater affinity for these fibres than other polar compounds. They suggested that the hydroxylic compounds were adsorbed on localised sites as a monolayer by hydrogen bonding at the oxygen atoms or peptide groups. Since water and methyl alcohol give similar isotherms on nylon, they also concluded that the sites of adsorption in nylon are same for both these vapours. The crystalline structure of wool was also found to be broken down by phenols with rise in temperature, though complete dissolution was not observed.

The present investigation was undertaken to determine whether vapour phase adsorption can help to indicate the physical state or location of dye in air dry fibres and also to determine the effect of the size of vapour molecule on the rate of adsorption, about which very little is known. Dyes are probably adsorbed from the aqueous bath in a monomolecularly dispersed state, but removal of water during subsequent drying disturbs the balance of forces between dye, fibre and solvent, and so aggregation of the dye inside the fibre probably occurs, especially with more colloidal dyes. Astbury and Dawson[36] found by X-ray spectrography that wool dyed with Solway Blue SEN and Solway Blue B contained free dye crystallites oriented roughly along the length of the fibres. No evidence of crystallites was found in the case of the two other dyed fibres they examined which contained Orange II, a crystalloidal dye and Coomassie Blue 2RN, but amorphous aggregates, if present, would presumably remain undetected.

Experimental

Apparatus: The apparatus constructed for the investigations was based on the spring balance principle of McBain and Bakr[37]. It is diagramatically shown in Fig. 1. The essential parts are the adsorption chamber, which houses a sensitive Pyrex glass spring, a manometer, a liquid tube which houses a small glass bulb filled with the liquid whose vapours are to be adsorbed, a McLeod gauge for measuring the vacuum in the system, and a vacuum pump.

The adsorption chamber was approximately 35 cm. long and 4 cm. in diameter, and in this a Pyrex glass spring (13-15 cm. length) was suspended on a hook. On the lower end of the spring the sample of the fibre to be studied was suspended. Pyrex glass springs have been shown to be very satisfactory for these experiments[38]. The adsorption chamber was connected on one side to the liquid tube and the McLeod gauge and to the manometer and vacuum pump on the other.

The manometer was of ordinary U-tube type of uniform diameter, with a special one-way valve which can either connect both the arms of the manometer to the adsorption chamber and vacuum pump, or it can cut off one arm from it.

The liquid tube was a small chamber (c.a., 15 cm. in length and 2.5 cm. diameter) into which was placed a small thin glass bulb, containing the liquid, with a piece of iron resting on the bulb. The iron could be raised and dropped on the glass bulb, by a magnet, thus breaking the bulb and releasing the liquid into the tube.

The /...

The measurement of high vacuum was made on the McLeod gauge. This is a standard apparatus supplied by W. Edwards and co., London. It is connected to the vacuum pump through the adsorption chamber, and works on the simple principle of compressing the known volume of gas in a capillary tube, which is graduated, and the vacuum attained in the system can be easily read off.

The vacuum pump was supplied by N. G. N. Electrical Ltd., and has a single unit in which a rotary pump and an oil diffusion pump (A.O.P. 25, acting as a backing pump) are coupled together. The vacuum attained by the rotary pump alone is about 10^{-1} to 10^{-2} mm. of mercury, but with the oil diffusion pump connected, a vacuum up to 10^{-6} mm. of mercury could be obtained.

The assembly was supplied with stop-cocks and joints at suitable places, making it possible to connect or to isolate various parts in the system. The adsorption chamber, manometer and liquid tube are enclosed in an air thermostat, the temperature of which could be controlled within accuracy of $\pm 0.1^{\circ}\underline{C}$. They were mounted on a rigid stand constructed on the wall thus making it free of vibrations from the floor. The air thermostat was also provided with a fan which helped to circulate air and so attain a uniform temperature. All the stop-cocks and joints were of standard type specially designed to stand high vacuum, and a special vacuum silicone grease (Silicone High Vacuum Grease, by Edwards High Vacuum Ltd., Crawley) which is resistant to most chemicals and capable of standing high temperature was used.

Adsorption /...

Adsorption Technique: The experiments were mainly carried out to measure the rate of adsorption of different vapours on wool dyed with different dyes. The usual experimental procedure was as follows. The Pyrex glass spring was calibrated accurately against known weights, the extension of the spring having been measured by a cathetometer, and a calibration curve was obtained.

The fibre sample (0.24-0.28 gm.) was then mounted on the lower end of the glass spring and the air thermostat was brought to the desired temperature. The glass bulb was filled with the required liquid and was placed in the liquid tube with the iron piece in place. The whole assembly was then subjected to vacuum and the fibre was degassed at about 10^{-2} mm. of mercury and kept under that vacuum overnight at the temperature of the experiment. The vacuum was then raised to 10^{-4} mm. of mercury and the fibre sample was degassed for a further period of 3-4 hours, after which no further change in weight was noticed. The stop-cocks S_1, S_2 and S_3 were then closed and the manometer valve was turned so that only one arm of the manometer was in connection with the adsorption chamber. The glass bulb containing the liquid was then broken and the stop-cock S_2 was slowly opened so that the vapours of the liquid entered the adsorption chamber and the manometer. The extension of the glass spring was then measured at regular intervals of time by means of a cathetometer, and the total amount of adsorption (expressed as mmoles/gm.) was calculated for various times.

All the experiments were carried out at 35°C, and at the saturated vapour /...

vapour pressure of the liquid employed.

Attainment of High Vacuum: Many difficulties were encountered in attaining a high vacuum and holding it during the test period, which sometimes was as long as 60-70 hours. To overcome these difficulties, the number of joints in the apparatus was reduced to a minimum and in all the connections rubber joints were avoided. Application of grease with the fingers to stop-cocks and joints was also avoided, this being done by evenly spreading the grease on the clean joint by a thin glass rod. Before every set of experiments was started, the glass assembly was heated gently by moving a small flame over it, while the evacuation was in progress. This helped in removing the condensible gases in the apparatus, which would otherwise present difficulties in attainment of high vacuum. Once these precautions were taken the attainment and maintenance of high vacuum was much easier.

Accuracy and Reproducibility of Results: The limit of accuracy attained was quite good. A typical glass spring used in the present experiments had an extension of 14.6 cm. per gm. The cathetometer used for measuring the length of the spring could read 0.001 cm. which corresponds to 6.848×10^{-5} gm. of load. A load of 0.25 gm. could be safely used, so that an adsorption of 1% on the weight of the adsorbent, corresponding to an extension of $0.0025 \times 14.6 = 0.0365$ cm. Since the possible error in this measurement is 0.002 cm. the percentage error in measuring as low an adsorption value as 1% is about 5.4%. But since the expected adsorption was not less than 2%, a maximum error of about 2.7% was expected,/...

expected, at low adsorption, falling with rise in adsorption e.g., to 0.18% at 30% adsorption. This is sufficient for the purpose of present experiments.

The results presented are often replicates of three or four adsorption tests, made to test the reproducibility of the results. It was observed that the rate in the initial stages often varied slightly, but the final or the equilibrium adsorption values were always highly reproducible.

Adsorbents: Root ends of Lincoln fleece wool were cut and were Soxhlet extracted for 24 hours with methylene chloride, then washed in de-ionised water, steeped overnight, and dried at room temperature. Australian merino wool was also cleaned in a similar fashion.

Adsorbates:

Water: De-ionised water was distilled from a Pyrex glass distillation flask.

Methyl Alcohol: Pure methyl alcohol was redistilled just before the use.

Ethyl Alcohol: Spectroscopic quality alcohol, stored in a dry place, was used.

n-Propyl Alcohol: Distilled alcohol was redistilled just before the use.

Dyes: Dyes used were Solway Blue BN (C.I. 63010) (I.C.I.) and Irgalan Brown 2GL (C.I. Acid Brown 44) (Gy.). Solway Blue BN was applied to wool from a dyebath containing excess of dye, 15% glauber's salt and 3% sulphuric acid while Irgalan Brown 2GL was applied from a dyebath containing excess of dye and 3% ammonium sulphate. After dyeing the wool /...

wool fibres were washed thoroughly in water and dried at room temperature. The concentration of the dye in wool fibres was found out to be 8% for Solway Blue BN and 9% for Irgalan Brown 2GL.

Silver Chromate-containing wool was prepared by treating the fibre with excess of potassium dichromate and precipitating silver chromate inside the wool by treating it with excess of silver nitrate in solution. The treated fibre was washed overnight and dried at room temperature.

Results and Discussion

Before attempting any discussion on the rate of adsorption of vapours it should be stressed that the rate of uptake of any vapour by a porous adsorbent is affected by many factors. In the present work, the adsorbent being same in all tests and the adsorbate vapours having similar kinds of active groups, the rate, and the equilibrium adsorption value, will mainly depend on two factors, viz., the size of pores relative to the adsorbate molecules and the heat and energy of activation of the adsorption process. Both affect the rate of adsorption, and the former is responsible for the saturation adsorption, i.e., the saturation adsorption value will be mainly dependent on the diffusion of the vapour molecules.

Thus the rate of adsorption of water, methyl alcohol, ethyl alcohol and n-propyl alcohol vapours on clean wool, and on Lincoln fleece wool containing Solway Blue BN, Irgalan Brown 2GL and silver chromate, at saturation vapour pressure and at 35°C were studied. The typical rate curves for methyl alcohol are shown in Fig. 2. The saturation adsorption values for these rate tests (expressed as mmole/gm. of fibre) when plotted against the molecular weight of the adsorbate show a relation illustrated in Figs. 3, 4 and 5. It is seen that as the molecule of the alcohols becomes larger both the rate of adsorption and the equilibrium adsorption fall. This must be almost entirely due to the increasing molecular volume, because the adsorbates have similar active groups. The adsorption is expected to be due to hydrogen bonding of the hydroxy groups of the adsorbate with suitable groups in the/...

the wool and thus the expected orientation will be end-on. The cross-sectional area of different adsorbates in this orientation is almost the same, so that the only cause of the differences in adsorption is the relative size of the pores in adsorbent and the molecules of the adsorbates. This hypothesis is supported by the fact that there is a regular relation between the amount adsorbed at saturation and the molecular weight of different adsorbates (Figs. 3, 4 and 5).

Effect of Presence of Dyes on Vapour Adsorption: Larose[26] observed a reduction in the uptake of water vapour when wool was dyed with an acid dye, which led him to conclude that the sites of adsorption in wool, for an acid dye, and water vapour are the same. This reduction was also observed in the present work (Figs. 3, 4 and 5) in wool dyed very heavily with an acid dye, a metal-complex dye or containing silver chromate. If the adsorption sites for the dye and the water or alcohol vapours were the same, then at a high concentration of dye suchas used in the present work, it would be expected that no vapour should be adsorbed at all, since all the available sites would have been occupied by the dye. Instead it is seen that, while dyed wool does show consistently lower amounts of vapour to be adsorbed at saturation, the difference is very small, which would suggest that the aggregates of dyes are restricting the movement of vapour molecules to a certain extent. This reduction in adsorption at saturation by dyed fibres is a maximum with smaller vapour molecules and a minimum with n-propyl alcohol. If one assumes that this reduction is due to physical blocking of pores in /...

in the fibre by aggregated dye, it would be expected that since the water molecule is the smallest of those used, it will have a larger region in the fibre accessible to it and hence more chance of meeting an aggregated dye particle, compared with n-propyl alcohol, which can enter only a limited number of pores and hence has less chance of meeting such a particle, thus showing the least reduction in the saturation adsorption value.

Pore-size Distribution in Wool: Speakman[39] has suggested that the maximum pore diameter in wool is about 6Å, this being determined by the fact that n-propyl alcohol is adsorbed while n-butyl alcohol is not. There has been some disagreement[40,41] regarding the penetrability of wool fibres by the larger molecules of alcohols etc., but it seems to be fairly well established that the rate of penetration of a molecule as large as n-butyl alcohol under normal conditions is so low that the fibre may be considered inpenetrable to it, and the normal pore-size may be estimated accordingly. Recently Quynn[42] has determined the pore-sizes in different fibres by the high pressure mercury porosimeter and claims to have measured pores down to a minimum size of 150Å. This very large difference from the results of Speakman is hard to understand. But on the basis of the present results the author agrees with the figure suggested by Speakman. The results obtained by Quynn are doubtful because the method requires pressures up to 15,000 psi to be applied in order to make the mercury penetrate the pores, and it is very likely that at such high pressure the pores of a soft material such /...

such as a fibre are burst apart, leading to higher apparent pore-size values.

Having thus established the maximum pore-size in wool as about 6Å, an attempt was made to estimate the pore-size distribution. If it is assumed that water vapour has all possible sites accessible in the amorphous region of the fibre, it is possible, from a knowledge of the size of the adsorbate molecule and its saturation adsorption, to calculate the percentages of accessibility for the different alcohol vapours and hence the ratios of different pore sizes. The results are shown in Tables I and II.

It is obvious that penetrability depends either on the volume or on the length, rather than on the cross-section of the alcohol molecule, because all the alcohols used have the same molecular cross-section, and therefore if they entered the fibre end-on and linearly extended they would all meet with the same resistance. We can therefore assume that the resistance of the pores to a bombarding long-chain molecule causes it to crumple to the folded form, and the diameter of this form is the value used in calculating pore sizes. These sizes however must be considered only approximate minimum values; since we do not know how much larger than the vapour molecule a pore must be before the molecule can just enter.

Differences between Varieties of Wool: In order to compare the different varieties of wool with respect to vapour adsorption rates, some experiments were also done with Australian merino wool. The results presented /...

presented in Fig. 6 indicate that the adsorption properties of Lincoln fleece wool and merino wool are slightly different. It is seen that in merino wool the saturation adsorption of water vapour is slightly higher than on Lincoln fleece wool, while it is the same on the two fibres for methyl alcohol vapours but progressively less for ethyl alcohol and n-propyl alcohol. Measurements of external surface area (diameter readings on "Megascope") of these two fibres showed, as expected, a slightly higher surface area for merino wool (1080 $cm^2/gm.$) compared with Lincoln fleece wool (945 $cm^2/gm.$). These results indicate that the higher saturation adsorption of merino wool for water vapour cannot be due merely to the larger external surface, but must be due to an increase in internal surface area, since most of the active sites in the amorphous regions will be accessible to water vapour molecules, because of their small size. As the adsorbate molecule becomes larger, the saturation falls in merino wool more rapidly with increase in molecular size than in Lincoln wool. This indicates that simultaneously with reduction in diameter of the wool there is a reduction of pore-size. Thus the larger the adsorbate molecule becomes, the lower its saturation adsorption value, as compared with Lincoln wool.

PART II

SOME ASPECTS OF THE KINETICS OF DYEING WOOL AND GELATIN

Introduction

This part of the thesis describes a series of experiments carried out to study the comparative rates of dyeing of different series of dyes on wool and gelatin, and thereby to study the influence of dye structure and other factors on the rate of dyeing. Some experiments were also performed to investigate the effect of certain solvents in the dyebath on the rate of dyeing of wool, a topic which has aroused considerable interest in recent years.

The dyeing of protein in a solution of low pH is mainly an ion-exchange process in which the dye anion slowly replaces a small inorganic ion being held as a geganion to the charged amino groups of the protein. The kinetics of base exchange has received much attention[43,44], and in most cases it has been shown that the rate of exchange is governed by the uniform diffusion of ions through the solid phase.

The forces linking acid dyes to proteins are, in the following order of importance. (i) Ionic forces between the ionised groups of opposite charge in the dye and in the fibre. The importance of ionic charge in the dyeing of proteins with acid dyes is very clear, as it is well accepted that the dyeing of wool in acid solution is largely an ionic process. Hydrogen ions are adsorbed from the solution, and the dye anions are then taken up to produce electrical neutrality. (ii) Van der Waals forces between the hydrophobic parts of the dye and the fibre, varying with the area of the dye molecule or approximately as /...

as the molecular weight. The fact that dyes are adsorbed to a greater extent than inorganic ions indicates the presence of additional attractive forces between dye and fibre, which must be mainly van der Waals forces. Furthermore, if wool is immersed in neutral or slightly alkaline solution it takes up a negative charge and consequently repels anions. If an anionic dye is dependent for its affinity for wool on ionic forces, it will clearly fail to dye the fibre under such conditions. This is in fact the case with levelling acid dyes. The electrical repulsion can be overcome ifthe dye has considerable non-ionic affinity for the fibre, as in the case of milling and "Carbolan" dyes. (iii) Co-ordination forces or hydrogen bonds between specific groups in the dye and the fibre. No definite evidence of interaction of dyes with chemical groups in wool apart from ionic groups has yet been obtained, but some such interaction involving hydrogen bonding is believed to occur[45], for if this were not so, all dyes of the same degree of sulphonation should vary in wash fastness in direct proportion to their molecular area. In fact hydrogen bonds have been detected by Chipalkatti et al.[5] when they studied the adsorption of aliphatic and aromatic non-ionic compounds on nylon and wool in absence of water. This idea is also emphasised by Valko[46].

Diffusion Mechanism

Three distinct stages have been recognised[47] in the process of dyeing textile fibres from an aqueous dyebath. In the first stage, the dye molecules are transported to the fibre-water interface by a combination /...

combination of aqueous diffusion and mechanical stirring or agitation of the dyebath. The dye molecules are then adsorbed on the outer surface of the fibre. The final stage is the diffusion of the dye inside the fibre until the dye concentration is uniform throughout the fibre phase.

Diffusion phenomena of dyes in natural and synthetic polymers have been studied by a number of workers. Some of the polymers, e.g., cotton and wool, seem to have attracted more attention than others, while there appears to be very little work reported on gelatin, though undoubtedly the subject must have been studied in the photographic industry. Different workers have used different equations for the calculation of diffusion coefficient. The equation given by Crank[48] for a semi-infinite medium, when the boundary is kept at a constant concentration Co is -

$$C = Co \ \text{erfc} \ \frac{x}{2\sqrt{Dt}}$$

where erfc is the error function complement, C is the concentration of diffusing substance, x is the space coordinate measured normal to the section, t is the time of experiment and D is the diffusion coefficient.

The above expression shows that the solution of the problem of diffusion into a semi-infinite medium having zero initial concentration and the surface of which is maintained constant, involves only the single dimensionless parameter $\frac{x}{2\sqrt{Dt}}$

It follows from this that:

1. /...

1. the rate of penetration at any given concentration is proportional to the square root of time;
2. the time required for any point to reach a given concentration is proportional to the square of its distance from the surface and varies inversely as the diffusion coefficient;
3. the amount of diffusing substance entering the medium through unit area of its surface varies as the square root of time.

Sumner[49], in studying the rate of diffusion of reactive dyes in cellulose applied the equation of Danckwerts to his results. The equation is of the form -

$$Q = C\sqrt{Dk}\ (t + \tfrac{1}{2}k)$$

where Q is the amount of dye diffusing through unit area of surface, which in this case is equated with the amount of dye fixed, C is the equilibrium surface concentration which can be calculated from the thermodynamic affinity, D is the diffusion coefficient, k is the reaction constant of dye with cellulose and t is the duration of the experiment.

Speakman and Smith[50] used Hill's equation in their study of diffusion of dyes into animal fibres, according to which, when a semi-infinite solid is brought into contact with a large quantity of well stirred liquid containing a diffusible substance of concentration Yo, the total amount diffusing across unit area of the boundary in time t is -

/...

$$A = 2Yo\sqrt{\frac{kt}{\pi}}$$

where k is the diffusion coefficient. In the case of dyeing the same equation is valid so long as Yo remains constant, and the diffusible substance does not reach the axis of the fibres.

Three mathematical papers[51,52,53] dealing with the problem of diffusion of a finite amount of diffusing substance into a cylinder may be mentioned. In these papers dyeing has been considered as a process of diffusion along capillaries accompanied by adsorption on the walls of the capillaries. Hence the dye is considered to exist in the fibre in two states, adsorbed state and mobile state, the concentration of these two being related by the adsorption isotherm between solution and the fibre. It was observed by Alexander and Hudson[54] that the shape of the kinetic curve predicted by this theory did not agree with the experimental curve, except in the initial stages of the process. This diffusion-with-adsorption theory of Crank[52] and Wilson[51] assumes a continual equilibrium between the dye in solution and the dye on the fibre, which will depend upon instantaneous adsorption and desorption. This disagreement over the theoretical and experimental rate curves indicates that the rate of adsorption in the later stages of the process is much greater than the predicted rate, and is explained by Alexander and Hudson[54] thus: in the course of a kinetic experiment a state of apparent equilibrium is reached with most of the dye adsorbed on the outer portion of the fibre, which is followed by redistribution of /...

of the dye throughout the whole of the fibre leading to thermodynamic equilibrium. In this course of redistribution, a readjustment in the concentration of dye in solution occurs, but this change is small compared with the change in concentration which occurs during adsorption, owing to the very high value of the distribution coefficient. This idea is, in fact, supported by the work of Morton[55] and Royer et al.[56] who have produced photomicrographs from which it is seen that a thick deposit of dye is confined to an outside film of the fibre during the time taken for a kinetic determination, the subsequent equilibrium requiring several days.

The semi-empirical treatment of Wilson and Crank is based on the assumption that rapid adsorption occurs at specific sites, and removes the dye from the sphere of diffusion. It considers the diffusion front to proceed in the form of a well defined band with complete saturation with adsorbed dye of the volume penetrated at the higher concentration. It suffers from the postulate that the concentration of free mobile dye within the fibre is equal to that of the bath concentration. This is probably not true owing to the membrane effects,[57,58,59] although the two concentrations would be expected to vary proportionally as a first approximation.

The above discussion suggests that only a part of the dye within the fibre is mobile and governs the rate of diffusion. It is argued by Alexander and Hudson[54] that the diffusion through the wool structure may occur in one or two ways. The fibre may either be considered as

a /...

a homogeneous gel of relatively low water content, or as a heterogeneous system of solid phase penetrated by innumerable pores of relatively large diameter, compared with molecular dimensions, which are filled with solvent held by capillary attraction. Diffusion in the latter system would proceed through the macropores, with a velocity comparable to that in a purely aqueous phase, and the majority of the dye ions would be adsorbed on the pore surface and would not participate further in the diffusion process. If this were true, it is difficult to account for the high activation energy of 13 kcal./mole. as obtained by these workers, compared with the value of about 5 kcal./mole. of dyes in aqueous solution by Valkó[46]. In a similar system Boyd and coworkers[43] showed that diffusion of ions through a resin swollen to an extent similar to wool fibres is not controlled by diffusion in the macrapores, but by diffusion through solid.

The high activation energy obtained by Alexander and Hudson[54], as argued by them, would suggest that diffusion requires deformation of the keratin structure with hole formation, as also suggested by Neale[60], which could be the case only if the ions diffused through pores of molecular dimension. A process of this type can not be regarded as a two-phase diffusion, and it becomes equivalent to migration of ions through the swollen fibre structure, which is regarded as a uniform gel of low water content. This idea is also supported by the work of Booth[61], who showed that very simple ions require a high activation energy of approximately 10 kcal./mole., even though they would be expected /...

expected to be highly mobile within the fibre.

Kinetics of Dyeing

Existing data on the diffusion of ions in proteins immersed in aqueous electrolyte solution is quite adequate, but most of the work in this field is confined to one particular dye or simple organic and inorganic compounds, and very little information regarding the relative rates of dyeing of analogous series of dyes is available.

Sheppard et al.[62] have studied the diffusion of dyes into gelatin, using both acid and basic dyes. They concluded that for a relatively dilute solution of acid and basic dyes, gelatin takes up the dye according to a reversible reaction between protein cation and dye anion for the former, and protein anion and dye cation for the latter. The binding is by electrostatic forces, and the equilibrium or the distribution of the dye between the bath and the protein is governed by the pH, the neutral salt content and the concentration of the dye according to the Donnan membrane equilibrium.

In similar work on animal fibres, Speakman and Smith[50] found with Acid Orange 2G that the amount of dye adsorbed was a linear function of the square root of time, despite the falling concentration of the bath and they attributed this to the diffusion of dye taking place from a layer of dye solution of constant concentration at the fibre surface. They also observed that fine diameter fibres adsorb dye at a greater rate, and also that the temperature at which successful dyeing can be carried out is an inverse function of the degree of dispersion of the dye /...

dye. Alexander and Hudson[54] using the same dye on wool showed that diffusion takes place either through a thin film of immobile liquid surrounding the fibre or through the fibre. It was shown that at low concentration of dye, the diffusion of dye through an unstirred film of liquid is the slower of the two processes, whatever the degree of agitation, but at higher concentration the rate controlling step changes from diffusion through liquid film to diffusion through solid when the stirring of the solution is increased beyond the point at which the reaction becomes stirring independent and the activation energy, determined from the temperature coefficient, changes from approximately 5 to 13 kcal./mole.

Speakman and Smith[50] also found an increase in dyeing rate with decreasing pH. Peters and Lister[63] using the same dye have confirmed the above results. They calculated the diffusion coefficient of the dye within the fibre and found it to be independent of pH at least up to a temperature of 60°C. The increase in rate of dyeing is attributed, therefore, to the increase in surface concentration with decreasing pH. At higher temperatures the rate of agitation is believed to be the rate determining factor.

The importance of the surface structure of wool in determining the kinetic properties has received much attention. Speakman and Smith[50] found that the cuticle scales in wool offer a considerable resistance to the penetration of dye. Millson[64] has supported this observation and showed with photographic evidence that the dyeing first occurs at the /...

the outer edges of the scales and that physical distortion of the fibre affected the penetration of the dye to a great extent. Similar effects have been explained on the existence of a very thin membrane of low permeability discovered by Gralén and his coworkers[65], who call it "epicuticle". This membrane offers great resistance to the diffusion of dyes or even simple acids, but is easily damaged by various normal processing treatments. Consequently, the rate of dyeing of a wool fibre is critically dependent on its pretreatment. Lindberg[66] was able to show that when wool was treated with alcoholic potash the diffusion coefficient increased very rapidly in the initial stages followed by a slow increase, suggesting that the epicuticle is destroyed by such a treatment. Similar results were obtained by Lemin and Vickerstaff[67] who found that chemically modified wool adsorbed dye more rapidly than normal wool, the order being alkali damaged > chlorinated > peroxide bleached > carbonised > normal wool. The increased rate of dyeing as obtained by Lindberg[66] and Lemin and Vickerstaff[67] could also be partly due to the breakdown in disulphide linkages during chemical treatments, which agrees with the observation of Speakman and Smith[50] who observed an increase in resistance to dyeing with increase in the sulphur content of the fibre.

To study the influence of dye structure on the kinetics of wool dyeing, Vickerstaff[47] applied milling and levelling acid dyes to wool at the boil from aqueous dyebaths containing 3% sulphuric acid, 3% acetic acid and no acid respectively. The simple acid dyes were adsorbed more /...

more slowly than the fast-to-milling dyes, particularly at higher pH values. The fast-to-milling acid dyes, however, were adsorbed rapidly and unevenly from dyebaths of low pH, but were also adsorbed to an appreciable extent from neutral solution. This effect could be explained in terms of the higher molecular weights of dyes of this class, which agrees very well with the suggestion of Meggy[68] according to whom the affinity of a dye for wool depends mainly on the size of the hydrocarbon skeleton. He suggests that the affinity of acid dyes for wool is largely due to the fact that the bulk both of the dye molecule and of the wool fibre is hydrophobic, and that on dyeing the two hydrophobic surfaces can come together with a reduction in potential energy. Thus dyes of high molecular weight will have an affinity for the fibre independent of pH and consequently will be adsorbed from neutral solutions. These results are confirmed by the work of Alexander and Charman[69] who found that Carbolan Crimson B had a greater affinity as compared to Azo Geranine and this must be due to the long hydrocarbon chain in case of Carbolan Crimson B since this is the only difference between the two dyes, and because the paraffin chains in the dye have no hydrogen atoms available to form hydrogen bonds. It was also concluded by these authors that the surface activity of the dye contributes substantially to its high anion affinity.

Townend[70], and Townend and Simpson[71] have studied the relative rates of dyeing of different series of dyes. With Naphthalene Red J, Naphthalene Red EA and Naphthalene Scarlet 4RS they observed that the dyes/...

dyes with increasing basicity gave decreasing rates. They connected the rate of dyeing with the chemical constitution of dyes, and particularly with the number and nature of their acidic groups. Nicholls[72] measured the desorption rates from alkaline baths of the same series of dyes and observed that increase in basicity considerably increases the rate of desorption, while with dyes of the same basicity those having higher affinity for the fibre are removed less easily. He also showed that the rate of desorption of acid dyes from wool is controlled by the relative magnitude of the forces of repulsion between the charged fibre and the dye anion and the forces of attraction, such as van der Waals, hydrogen bonds, etc., between fibre and dye.

Valko[46] has shown that the surface tension does not affect diffusion measurements, and that different levelling agents having the same surface tension, affect diffusion in different ways. By reducing the dye concentration and keeping the concentration of levelling agent the same, the diffusion speed was always reduced strongly. These rule out the possibility that porous plate is being affected by the adsorption of levelling agents.

The Effect of Solvents on the Rate of Dyeing

The current interest in the process where the rate of dyeing of wool is increased by addition of certain solvents to the dyebath, stems from the work of Peters and Stevens[73]. They observed that in aqueous dyebaths containing sparingly soluble alcohols, amines or phenols the rate of dyeing with acid dyes (particularly the neutral dyeing 2:1 dye-metal complex /...

complex dyes) was much more rapid than in the absence of these agents. For example, 4% Acid Black 58 was exhausted almost completely in 30 mins. at 60°C from a bath containing 7% n-butanol. The fastness to wet treatments of these dyeings was of the same order as that of the conventional dyeing which shows that adequate penetration of the fibre had been achieved. Lister[74] also observed a similar effect using o-dichlorobenzene in the dyebath as an emulsion. Delmenico[75] found that the inclusion of suitable solvents in the paste used in both melange printing and conventional printing of wool, greatly increases the rate of dye fixation and depth of colour. He found that the effect of solvent was less marked with chlorinated wool than with untreated wool, and from microscopic examination he observed that the new technique gave better penetration and distribution of dye than former methods. Beal et al.[76] have supported these observations and have suggested that chlorination to increase the rate of fixation of dye is not necessary when a solvent is present in the printing paste.

Kärrholm[77] has studied the effect of n-butyl and n-amyl alcohols in the aqueous bath at different concentrations of the alcohol, and observed that concentrations of alcohol lower than the saturation concentration did not affect the equilibrium exhaustion of the dyebath. The equilibrium exhaustion from the solvent saturated with water was, however, found to be lower than from an aqueous solution. Wool when pretreated with a solution of amyl alcohol in water for one hour at 60°C., rinsed and dried, and then dyed in normal way, showed an increase in the /...

the dyeing rate. In studying the effect of sulphonate groups in the dye, Kärrholm observed an increase in the rate of dyeing of a mono-sulphonated acid dye but a decrease in that of a tri-sulphonated acid dye. Examination of the influence of surface structure on the rate of dyeing in presence and absence of solvents revealed that the solvent produced a smaller increase in the rate of dyeing when chlorinated wool was used, compared with untreated wool, but there was still a large increase even with completely descaled wool.

Kärrholm also made a very interesting experiment in studying the rate of dyeing of Bromophenol Blue at two pH values. This dye was used because it has affinity for wool, is monomolecularly dispersed in solution and its dyeing rate is influenced by solvents in the dyebath. In addition, it exists in an acidic form at pH 1.2 whereas at pH 7.8 it exists in its basic form. It was observed that at pH 1.2 in presence of benzyl alcohol the rate of dyeing was increased while at pH 7.8 it was unaffected. It was also found that this dye had an exceptionally high partition ratio in benzyl alcohol when in acidic form as compared to the partition ratio in benzyl alcohol when in basic form. This led Kärrholm to believe that there was a connection between the rate of dyeing and the partition ratio of the dye in water and solvent phase.

Kärrholm and Lindberg[78] showed that the effect on the rate of uptake of acid dyes by woolis related to the partition ratio of the dye between the alcohol and water and that the rate of dyeing increases with decrease in the number of sulphonic acid groups in the dye.

Peters /...

Peters et al.[79] have studied the effect of benzyl alcohol and n-butyl alcohol on the swelling properties of wool and concluded that in aqueous solutions of alcohols no swelling occurred and at higher concentrations of alcohols, where the rate of uptake of dye shows maximum increase, there is slight suppression of swelling. These workers also calculated the heat of activation of 2:1 dye:chromium complex dyes, and found a tremendous reduction in the presence of benzyl alcohol, but the rate of dyeing did not increase in the expected proportion. This they attributed to the increase in the entropy activation barrier by the alcohol which partly counteracts the effect of the diminished activation heat barrier.

Beal et al.[76] studied the uptake of Irgalan Grey BL (C.I. Acid Black 58) in presence of benzyl alcohol to discover its effect on the concentration of solvent, pH, temperature, dye concentration, liquor to material ratio and presence of electrolytes. They showed that the rate of dyeing increased with the increase in the concentration of benzyl alcohol in aqueous phase, with decrease in pH, with increase in temperature, lower dye concentration, higher liquor ratio and increase in the amount of electrolyte in the dyebath. They also found, by comparison of dyeing in distilled water and tap water (c.a. 4^{o} hardness), that small amounts of calcium and magnesium ions produced appreciable increase in the rate of dyeing.

Hadfield and Lemin[80] have reported that the rate of uptake of highly anionic dyes, e.g., certain acid dyes and Procion dyes, by wool is /...

is increased significantly if benzyl alcohol is present in the dyebath with a cationic compound. They have shown that there is an optimum concentration of cationic compound required to produce the maximum effect and this concentration of cationic compound is related to the basicity of the dye.

Medley and Ramsden[81] have shown that preferential absorption of alcohols by keratin increases with the size of the hydro-carbon portion of the alcohol molecule, thus benzyl alcohol is absorbed much more than n-butyl alcohol or n-propyl alcohol. They also determined the diffusion rates of alkylbenzene sulphonic acids of general formula, R⟨⟩SO_3H, through keratin in presence and absence of 8% n-butyl alcohol. It was found that mobility in aqueous solution falls by a factor of about two for each methylene group in the side chain R, while in presence of solvent this decrease in mobility is considerably smaller.

The effect of the presence of solvents in the dyebath is also observed in polyamide fibres. Thus Siegrist and Hobday[82] applied selected anionic dyes to nylon in presence of benzyl alcohol and an anionic compound. The presence of benzyl alcohol greatly accelerated the rate of dyeing while the anionic compound promoted an even distribution of dye thus bringing about level dyeing.

The evidence presented above has given rise to three main theories to explain the accelerated rate of dyeing of acid dyes on wool in presence of an organic solvent.

The first theory was put forward by Alexander and Stacey[83] who suggested /...

suggested that the solvents act as a hydrogen-bond breaker, thus disaggregating the dye micelles even at room temperature, with the result that dye will be present in a monomolecularly dispersed state in solution, making it easy for the dye to penetrate into the fibre. This would account for the accelerated rates of dyeing.

According to the second theory[73] a layer of solvent is formed at the surface of the fibre and since the dye has preferential partition in the solvent, there is higher concentration of dye in this surface layer. This solvent-rich phase thus produces a high surface concentration gradient which leads to a higher rate of dyeing than it would from simple aqueous solutions. Dyeing can, therefore, be carried out at much lower temperatures than those normally used with aqueous dyebaths, where high thermal energy is needed by the dye molecules to overcome the energy barrier of the wool-water interface.

The third theory[84] assumes that the solvent modifies the fibre in some way so as to facilitate the uptake of dye, as in the "Carrier" method of dyeing synthetic fibres. According to this theory the solvent is adsorbed by, and precedes the dye into, the fibre, where the internal bonds are ruptured or loosened, thus facilitating the diffusion of dye.

It has also been suggested[85, 86] that solvent when present in the dyebath removes some matter from the fibre surface and interior, such as grease or fatty acids, thus increasing the permeability of the fibre and so to a faster rate of dyeing.

Experimental

Preparation of Substrates: Wool samples weighing 0.50 gm. were cut from a piece of scoured wool flannel and were thoroughly wetted in distilled water before entering into the dyebath.

The external surface area of the wool was calculated from the measurements of fibre diameter. This was done with the help of a projection microscope (Megascope) at a magnification of 500 times. A mean of 150 diameter readings was taken to ensure average results. The surface area thus obtained was 1.26×10^3 sq. cm. per gram (which compares well with the value of 1.4×10^3 sq. cm. per gram as obtained by Aickin[87], who used Australian merino wool).

Pieces of gelatin film weighing 0.50 gm. were prepared as follows. Slides of optical glass were cut to size 4" x $2\frac{1}{2}$" and 8 such slides were placed on a glass plate which was mounted on a metal frame above 4 electric lamps. The whole set-up was levelled by means of levelling screws. A 6% solution of gelatin (pure photographic quality) was prepared in distilled water, and 8 ml. of this solution was evenly spread over the slides, the lamps were then switched on to dry the gelatin solution mounted above. The drying operation took about 2 hours.

The plates when dried were removed and placed in a bath of 10% formaldehyde solution for about 2 hours to harden. The hardened gelatin film with the glass plate was then washed to remove the excess of formaldehyde and stored until required. One such plate was used for each test and the gelatin film was stripped off, before use, by immersion /...

immersion in hot water. The surface area of the gelatin film was calculated to be 256 sq. cm. per gram by the author's colleague[88].

Apparatus: The rate of dyeing was measured by progressively taking the optical density readings of the dye solution using a Unicam S.P. 600 spectrophotometer at the maximum absorption wavelength of the dye. The dyebath was an ordinary one-litre beaker and the dye solution was removed by means of a small pipette.

Procedure: The dyebath was made up to 600 ml. by taking the dye, 0.25 gm. of acetic acid and the required quantity of distilled water, thus giving a liquor ratio of 1200:1. Such a high liquor ratio was chosen to offset the losses due to evaporation and to give reproducible results. The amount of dye taken in each case was 25 ml. of 1 mmole. per litre dye solution. This concentration of dye solution, depending on the molecular weight of the dye, gave approximately 3% of dye on the weight of the material. The dyebath was heated to a temperature of 70°C ($\pm$0.5°C) and optical density was measured before entering the substrate, and then at regular intervals of time while the dyeing proceeded. The dye solution withdrawn for the optical density measurements was returned to the bulk after the optical density measurement. The temperature of the liquid in the cell during the optical density measurement was found to be 57°C. While the dyeing progressed, the dyebath was stirred gently by a glass rod at regular intervals of time. Some experiments were repeated at a later stage using a continuous dyeing apparatus described by Dandekar and Giles[89], and/...

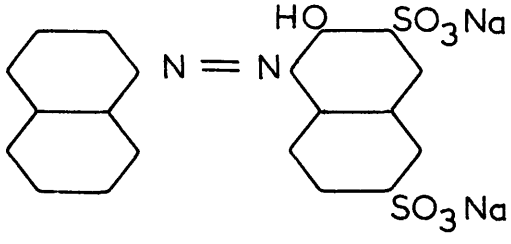
and the results were identical with those obtained by hand operations. To check on the reproducibility of the results, some of the experiments were also done by different operators and the results were found to be reproducible.

The experiments for measuring diffusion coefficients, where prolonged dyeing was required, were performed in a flask fitted with a water condenser.

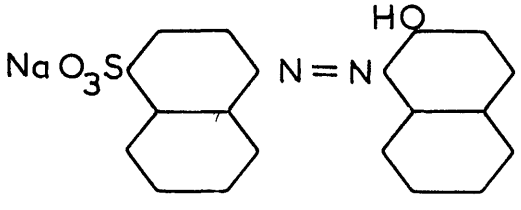
The molecular volumes of the dyes (not including the sodium ion) were measured by making "Catalin" molecular models of the dyes and immersing them in water in a graduated cylinder. The volume of the water displaced was noted and since the scale of the models was 1 cm. = 1 Å, the volume of water displaced in cubic centimeters corresponded to the volume of dye in cubic Angstrom units.

The following sets of dyes were used in the dyeing experiments.

Sulphonated Dyes

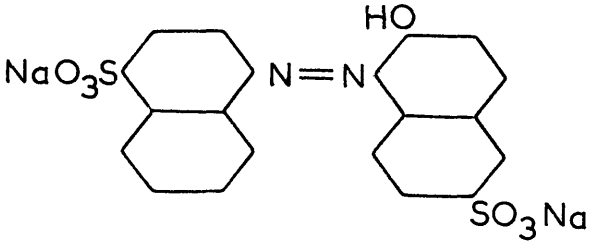
I. 

(∝-naphthylamine→R-acid)

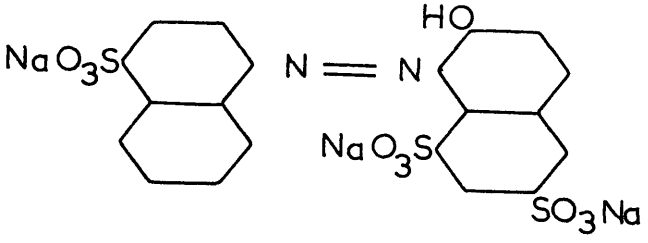
II. 

(Naphthalene Red J)
C.I. 15620

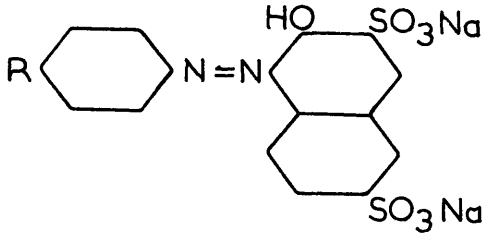
III /...

III. 

(Naphthalene Red EA)
C.I. 16045

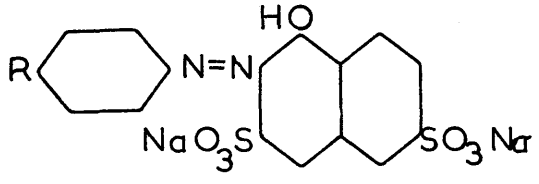
IV. 

(Naphthalene Scarlet 4R)
C.I. 16255

V. 

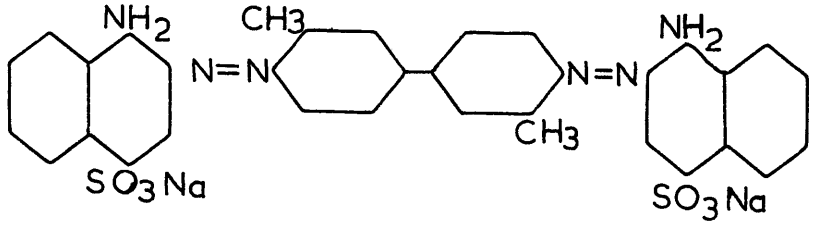
(aniline, etc.→R-acid)

a, R = H; b, R= CH_3; c, R = n-C_4H_9; d, R = n-$C_{12}H_{25}$

VI. 

(aniline, etc.→violet acid)

a, R = H; b, R = C_4H_9

VII. 

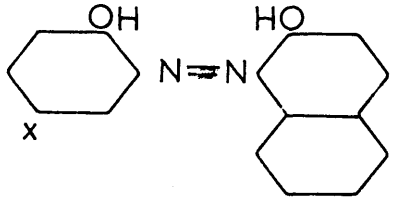
(Benzopur-purine 4B)
C.I. 23500

2:1 - Unsulphonated dye-metal complexes

VIII. Irgalan Orange RL (Gy.) (C.I. Acid Orange 86)

IX. Cibalan Red 2GL (Ciba) (C.I. Acid Red 211)

X, XI. Complex of chromium with two molecules of -



Complex X, x = H; complex XI, x = $-SO_2Me$.

(X, XI were supplied in pure form by Dr. G. Schetty of Geigy Ltd., Basle).

The azo acid dyes were recrystallised several times from suitable solvents until the extinction coefficient was constant. The Irgalan and Cibalan dyes were commercial dyes and X and XI were pure laboratory samples. Distilled water was used for all the tests. Benzyl alcohol was redistilled before use. Meso-inositol and D-glucose were pure commercial samples (B.D.H. Ltd.), and dioxan was of "specially dried" (B.D.H. Ltd.) quality.

Results and Discussion

All the data on rate of dyeing are summarised in Table III. The values for $t_1^{\frac{1}{2}}$ and $t_2^{\frac{1}{2}}$ are determined from the times representing the linear portion of the rate curves, shown with corresponding exhaustion values (Exh_1 and Exh_2) of the dyebath.

According to Speakman and Smith[50], since the process of dye adsorption by animal fibres is one of simple diffusion from a surface film, it is possible to give numerical expression to the rate of adsorption by calculating the slope of the line obtained by plotting the colorimetric readings against $t^{\frac{1}{2}}$ where t is the time (in minutes) from the start of dyeing. Here optical density readings from spectrophotometric measurements are converted to the percentages of the original readings, in order to make the values for different dyes comparable. These values are then plotted against $t^{\frac{1}{2}}$, giving linear plots (Figs. 7,8) for dye diffusion into the fibres. The slopes of these rate curves are then divided by the external surface area of the substrate, as was done by Speakman and Smith[50], and the numerical values so obtained (here called the "relative dyeing rates") are plotted against the number of added substituent groups attached to each dye in the series (Figs. 9,10), and also against the molecular volume of the dye (Figs. 11,12).

Characteristics of Rate Curves

In the present tests, in all the cases, the plots of the percentage of dye unadsorbed against $t^{\frac{1}{2}}$ are linear over a limited range of time (Figs. /...

(Figs. 7,8). There is, however, an initial period of about 2-4 minutes during which the rate of dyeing steadily increases to the value maintained over the linear portion of the curve. This initial "induction period", which occurs both in wool and gelatin, may represent the time taken for the dye molecules to come in close proximity to the substrate and build up a concentrated surface layer from which the dye subsequently diffuses into the substrate. This effect is also observed in the data of Medley and Andrews[86], and they have attributed this effect to the surface barrier presented to the dye molecules by the wool surface. Since the effect is observed in the case of both wool and gelatin, it is more likely to be due to the formation of a concentrated layer of dye on the substrate, which then acts as a constant concentration reservoir, whose presence accounts for the linear portion of the curve.

The rate curve for the dye Vd on wool is anomalous (Table III) in that it shows an initial very rapid rate, followed by a much slower rate over the linear portion of the curve. This initial rapid rate is attributed to the rapid build-up of a condensed monolayer on the outer surface of the fibre due to the highly surface-active nature of the dye. The subsequent lower rate is attributed to the much slower penetration of the dye in the internal pores of the substrate. The characteristics of this second portion fit remarkably well with the data presented for other dyes of the same homologous series (Figs. 9,11).

Relation between Rates in Gelatin and Wool

As previously mentioned, the effect of the different surface area of /...

of the two substrates is eliminated by dividing the slope of the rate curves by the external surface area of the substrate, thus enabling true comparison of the surface characteristics of the substrates. This then gives a true comparison of dyeing rates of different dyes on different fibres. The numerical value so obtained by dividing the slope of the rate curve by the surface area of the substrate is called the "relative dyeing rate", and when this rate is plotted for each dye on a logarithmic scale against the number of variable substituent groups or atoms in the dye molecule, and also against the molecular volume of the dye, good linear curves are obtained (Figs. 9,10,11,12). The plots for gelatin and wool for each series of dyes are almost parallel. Thus the true rate of dyeing in gelatin is always greater by a constant factor (about 4) than that in wool. However, the actual observed rate, that is the rate of dyeing obtained directly without taking into consideration the external surface area of the substrate, in gelatin is lower than in the wool samples used here. The higher absolute rate of dyeing in gelatin suggests a more porous structure for gelatin, perhaps with a larger average pore size, as compared to wool.

Effect of Substituent Groups and of Molecular Volume on Dyeing Rates in Various Substrates

The results obtained for wool and gelatin with dyes of varying basicity show that as the basicity increases the dyeing rate decreases proportionately (Figs. 7,8). Thus the increase in sulphonate groups has a retarding effect on dyeing, but if the diffusion rate depends on the /...

the affinity of dye for the substrate, i.e., if the greater the affinity the slower the rate of diffusion, this would disagree with the observation of Gilbert[90], according to whom the affinity decreases by about 1 kcal./mole. for each sulphonate group added.

Two explanations can be forwarded to explain the observed differences and either or both might be operative. (i) With increasing basicity, the size of the dye molecule and also the molecular weight of the dye increases, and this may outweigh the corresponding effect due to the decrease in affinity. A similar effect has been shown by Lemin[91], who found that affinity increases with increase in molecular weight, and is independent of the nature of the substituent groups. (ii) The increase in the number of sulphonate groups will increase the solubility of the dye in water, thus making it difficult for the dye to become adsorbed on the fibre because of the higher energy required to break the dye/solvent bonds.

Many workers have tried to relate the diffusion coefficient with molecular weight or molecular size of dyes. Thus in the case of disperse dyes on polyester fibres, a relation between the molecular size (as expressed by its maximum length x breadth x thickness) and the reciprocal of diffusion coefficient has been shown by Glenz and co-workers[92], while Sekido[93] has shown a relation between the molecular area of the dye molecule and the square root of diffusion coefficient, for films, but in both the cases there is a wide scatter of the results. A linear relation has also been found by Odajima[94] between the logarithm /...

logarithm of the diffusion coefficient and the square root of the molecular weight of the dye, for anthraquinone and azo disperse dyes on secondary cellulose acetate and for acid dyes in a copolymer of 6-nylon and 6.6-nylon. In the present results a linear relationship has been established between the number of substituent groups in the dye or the molecular volume of the dye, and the logarithm of the adsorption rate (Figs. 9,10,11,12). From this, it is clear that the geometry of the dye molecule, as well as the nature and number of the substituent groups determine the rate of adsorption on a given substrate. In most cases three dyes were used in each series and each series gives its own characteristic straight line. Thus R-acid dyes (Figs. 11d,12d) have lower rates than the Violet acid dyes or the Naphthalene Red series of dyes. When the molecular models of these dyes are prepared it is found that compared to other dyes the R-acid dyes are exceptionally wide at one end of the molecule due to the sulphonate groups protruding at this end. The structural features of all these dyes being similar except for the position of the sulphonate groups, the slower rates of the R-acid dyes can only be due to their greater width. In these dyes the end striking the substrate must play an important part in the ease of penetration into the substrate. In R-acid dyes, if the end with sulphonate groups strikes the substrate first the dye has less chances of penetrating into the substrate, because of its greater width, than it would have if the other end strikes first.

The effect of a large change in molecular volume without the change in /...

in degree of basicity is seen by comparing the results for dye VII with those for series V (Fig. 11). The large molecule of dye VII has a slower rate compared to the series V dyes. This shows that there is an increase in affinity with increasing molecular volume, which could be due to the increase in physical forces acting in the process of adsorption.

The dyes X and XI show an unusually higher rate of adsorption (Fig. 12) as compared to molecular volume, than the sulphonated dyes. This is probably due to the fact that both these dyes are unsulphonated. The ion-ion attraction between the sulphonate groups in the dyes and the cationic sites in protein in acid solution must exert a retarding effect on the movement of the dye molecules across the protein surface, and since these dyes have no sulphonate groups such a retarding effect is not possible. However, these two dyes have an ionic charge, which is located on the complexing metal atom, but on account of the peculiar shape of the molecule this charged atom cannot readily come into contact with cationic sites in the substrate and hence it is presumably almost inactive in influencing the rate of adsorption. The dye XI has two polar groups ($-SO_2Me$ groups), but they are not likely to exert a retarding effect because they are proton-accepting groups and proton-acceptors are known not to form hydrogen bonds readily with proteins[35,95].

The above discussion leads to the conclusion that with basicity remaining the same, the rate of adsorption decreases with increase in the molecular volume of the dye. This is logical if we consider at any /...

any moment individual dye molecules and dye micelles bombarding the substrate from the solution at every angle relative to the surface pores. One factor that determines the rate of adsorption is the proportion of dye molecules which happens to strike pores at an angle at which the dye can enter most easily. Obviously this proportion will be higher, the smaller the molecular volume of the dye and the more amorphous the substrate. Thus the constant proportionality of difference between rates in gelatin and wool, gelatin giving the higher rates, shows that gelatin has a higher average pore size than wool, and so a bombarding dye molecule has a better chance of entering a pore in gelatin than in wool. In the light of this argument it is also easy to understand the part played by the molecular volume of the dye, penetration being easier with the decreasing size of the molecule. The very high rate of adsorption of benzyl alcohol by wool from aqueous solutions (Fig. 13) on the basis of present results is clearly due to its small molecular volume and absence of ionic groups in its molecule. Its molecular volume is about 58$\mathring{A}^2$, and assuming this will fall on line C (Fig. 12) (because of its non-ionic nature), on extrapolating back the line to this molecular volume it is found that its adsorption rate will be about 6.6 times as great as that of the most rapid dyeing dye (II) tested here.

Affinity of Acid Dyes for Proteins

As mentioned earlier, the affinity of a dye for the substrate will tend to reduce the rate of transport of the dye into the fibre and also the/...

the rate at which the dye can be desorbed. The forces acting in this will usually be the dye-fibre attractive forces which will cause the dye molecules to remain attached to fibre molecules in the process of diffusion thus reducing the speed of the process of diffusion. It is thought[96] that dye-dye forces also tend to have a similar effect on the rate of diffusion. Nicholls[72] thus found that in acid dyes of the same basicity, the desorption rate from wool into alkaline buffer solutions falls with rise in dye-fibre affinity. He also found that the rate falls with reduction in basicity (Table IV), thus the fewer the sulphonate groups in a dye molecule the slower it desorbs into alkaline solution. This effect is explained by him as the result of repulsion between the anionic sulphonate groups and anionic charged sites in the fibre, that is negative affinity produced by the alkaline solution. The opposite condition should apply to acidic conditions, where there is positive affinity of sulphonate groups for cationic sites in the fibre, that is, the rate of adsorption should decrease with an increase in the number of sulphonate groups. In the present results this is found to be the case in dyes of the Naphthalene Red series (dyes II,III and IV). In the relationship between the molecular volume and the relative dyeing rate (Figs. 11,12) it is also seen that dyes II and Va have the same molecular volume, but dye Va dyes the more slowly. This could be due to the greater width of dye Va at one end, as stated before, but it could also be partly due to the retarding effect exerted by the extra sulphonate group, in reducing the rate of dyeing /...

dyeing of dye Va, even though the molecular volume of these dyes are the same. This supports the view put forward above that the affinity of a dye increases with the increase in its basicity unlike the view suggested by Gilbert[90].

Diffusion Coefficients in Wool

The method used in this work for measuring the diffusion coefficients was a similar one to that outlined by Vickerstaff[47] and used by other workers[86]. The method is best used for films where the thickness is uniform and can be measured accurately, but it is also recommended for fibres, provided the fibre diameter is measured fairly accurately and an average of many readings employed. The equation assumes a dyebath of constant concentration, and the ratio of the uptake of dye at a given time (C_t) to the uptake at saturation (C_α) is plotted against $t^{\frac{1}{2}}$, where t is the time from the commencement of dyeing (Fig. 14). The diffusion coefficient D is obtained from the slope, S, of the linear portion of this curve by the relation -

$$S = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2} \right)^{\frac{1}{2}}$$

where a is the average radius of the fibres. This equation has been modified by Medley and Andrews[86], when used for wool fibres, by introduction of a correction factor for the "surface barrier" effect presented by the nature of the surface of the wool fibres. This effect of a "surface barrier" is stated to be significant in the initial stages of the adsorption process and becomes progressively less /...

less significant as the adsorption proceeds. In the present calculations the wool fibre has been treated as a homogeneous cylinder and this effect is not taken into consideration, as the purpose of these measurements was merely to obtain data comparative with the rate measurements.

The diffusion coefficients for two sulphonated dyes (II and IV) were determined, and the values obtained were of the order of 10^{-8}cm^2/sec.; at 70°C. (Table IV). Considering the higher temperatures used in present experiments, these values are comparable to values obtained by other workers[54,63,97], who obtained values approximating to 10^{-11}cm^2/sec. at lower temperatures. These values are lower than the value of about 10^{-5}cm^2/sec. obtained for simpler molecules like hydrogen chloride[98] at lower temperatures. This difference, on the basis of present results, will be due to the size of the dye anion as compared to the size of the smaller HCl molecules. However, the values obtained in the present work bear the expected relation to the dye basicities and the adsorption rate (Table IV); the value of diffusion coefficient decreasing with increasing basicity and decreasing adsorption rate.

Relation between the Number of Atoms in a Dye Molecule and its Wash Fastness.

After having established a relation between the molecular volume of a dye and its rate of dyeing, it was decided to investigate if the size of the acid dye molecule has any significant relation to its wash fastness on wool. From the foregoing discussion it is clear that the /...

the larger the dye molecule the slower it penetrates into the substrate. It will thus be expected that the larger the dye molecule the slower will be its desorption during wash fastness tests and hence the higher its wash fastness.

To test this hypothesis, the structures and fastness of a variety of acid dyes were examined with the help of the Colour Index. The total number of carbon atoms and also the total number of atoms were counted. This will have a relationship with the molecular size. The wash fastness values plotted against the number of carbon atoms and the total number of atoms in the dye molecule are shown in Figs. 15, 17. These data were statistically analysed, the statistical analysis being presented in the appendix. It is seen that there is a relation between the number of carbon atoms and the total number of atoms, with wash fastness. The wash fastness increases with increasing number of atoms in the dye molecule. The results are highly significant statistically since the relationship accounts for 22-23% of the effect. The rest of the significance is due to other factors, perhaps, e.g., the crystalloidal and colloidal nature of the dye and its chemical nature.

Relation between the Number of Atoms in a Dye Molecule and its Migration Properties

From the foregoing it will also be expected that the larger the dye molecule the slower it will be in migrating once it is adsorbed by the substrate. To check this hypothesis the number of carbon atoms and the total number of atoms in the dye molecule were plotted against the /...

the corresponding migration number and the results are shown in Figs. 16, 18. There is a relationship between these, and as expected the migration number decreases with an increase in the number of atoms in the dye molecule. Statistical analysis, presented in the appendix, revealed that the results are highly significant, accounting for 21-26%, the rest of the significance being due to other factors.

Relation between Migration Number and Wash Fastness of a Dye

From the above it is clear that the higher the wash fastness the lower is the migration number and vice versa for a given dye. This is also found to be the case as shown in Fig. 19. These results are also statistically highly significant accounting for 30% of the effect.

Action of Solvents in the Dyebath

As mentioned before, some experiments were done to test the validity of various theories put forward to explain the observed increase in the rate of dyeing of wool with solvents in the dyebath. The experiments were arranged in such a manner that various theories could be tested, and for this reason in addition to the use of benzyl alcohol, other compounds, viz., dioxan, meso-inositol and D-glucose, were employed as solutes.

Benzyl alcohol, which is most commonly used in practice, is very rapidly adsorbed by proteins (Fig. 13), and since the mechanism is likely to be the hydrogen bonding of the hydroxy group in benzyl alcohol to the peptide groups in wool it presents a hydrophobic surface to the dye solution. It has a comparatively low solubility in water, some 4% by /...

by volume, and the spectrophotometric evidence (Table V) suggests that it has a disaggregating effect on the dyes in solution.

Dioxan is a solvent which also disaggregates the dye molecules in solution (Table V), but it will not be adsorbed by proteins[35,95] or nylon fibres since it is a proton acceptor. It is highly miscible with water.

Meso-inositol on the other hand has six hydroxy groups in its molecule and it is known to form hydrogen bonds with some proteins[95,99,100]. It has no large hydrophobic residue, unlike benzyl alcohol, and so when adsorbed as a monolayer by the fibre it will not present a hydrophobic surface to the dye solution. It has high solubility in water.

D-glucose has a ring structure like meso-inositol but is slightly different from it in its hydrogen-bonding properties. It forms[95,99,101] intermolecular hydrogen bond complexes with basic groups such as >NH, through the hydrogen of the aldehyde group in its open chain form, which is present in small proportion in aqueous solution. It does not form hydrogen bonds from aqueous solutions with other hydroxylic substances, or, usually, with the peptide group, because of the powerful water solvation of its hydroxy-groups.

Effect of Solvents on Rate of Dyeing

The rate of dyeing of three sulphonated dyes (II, III and IV) was measured in presence of 3%(v/v) benzyl alcohol in the dyebath, with other additions as before. It was observed that the rate of uptake of the monosulphonated dye II was much accelerated; while that of the disulphonated /...

disulphonated dye III showed only a slight increase. The rate for the trisulphonated dye IV, on the other hand showed a retarding effect in presence of benzyl alcohol (Fig. 9). Three 2:1 metal complex dyes (VIII, IX and XI) were also tested with similar concentrations of benzyl alcohol, and they also showed considerable acceleration in rates of dyeing as compared to the rates in absence of benzyl alcohol (Fig. 20 and Table III).

Dyes VIII and IX were also tested on gelatin and the dye VIII on nylon in presence of 3% benzyl alcohol by volume in aqueous solutions. It was observed that the accelerating effect occurs in gelatin (Figs. 21,23) and is almost as great as it is in wool; though nylon also showed a considerable accelerated rate of dyeing, the effect was not as great as it is on wool (Fig. 22).

The other solvents, dioxan, meso-inositol and D-glucose were tested with the metal complex dye VIII on wool (Fig. 20) at a concentration of 3% by volume in case of dioxan and 3% by weight of meso-inositol and D-glucose. It is seen that none of these solvents showed any accelerating effect on dyeing, but D-glucose and meso-inositol on the contrary showed a slightly retarding effect in the early stages of dyeing, in that the time before the $t^{\frac{1}{2}}$ plot becomes linear, is greatly extended. This suggests that they retard the build-up of the surface layer of dye on the fibre, perhaps by competition for some surface sites.

Effect of Solutes on State of Dye in Solution

It has been postulated[83] that organic solvents when present in the dyebath /...

dyebath as solutes disaggregate the dye micelles and thus bring about higher rates of dyeing. Spectrophotometric tests were done to detect whether in fact disaggregation is brought about by these compounds.

Absorption spectra of dyes in water were measured in presence and absence of the above mentioned compounds. Most dyes of all classes have two absorption bands in the visible region. These bands are tentatively identified with Lewis and Calvin's[102] and Lewis'[103], x and y bands because they are close together and vary as expected with concentration changes. Lewis and Calvin have suggested that the absorption spectrum of a substance with a planar or almost planar molecule should consist of bands corresponding to electronic oscillations along the three perpendicular axes of the molecule. With increase in the dye concentration either in solution or adsorbed in solid films, the dye will tend to aggregate and consequently cause disturbances in the electronic oscillations of the molecule. If the dye packs face to face there may thus be an increase in height of the band of shorter wavelength relative to those at longer wavelength. Thus the relative heights of the bands give a qualitative idea of the state of dye in the solution or in the substrate. This has been confirmed by many workers, e.g.,[104,105].

Table V and Figs. 24,25,26 show the effect of the different solutes upon the x - (monomer, long-wave) and y - (aggregate, short-wave) bands of some of the dyes used in here in presence and absence of solutes. The Procion dye was included in the tests for comparison because /...

because it has two very pronounced wave bands which are considerably affected by disaggregating solvents[106].

Taking the evidence from the results of the Procion dye tests, it is clear that both benzyl alcohol and dioxan are effective in bringing about the disaggregation of dye in solution, while glucose and inositol are ineffective. There is in some cases a slight shift of peak ("Solvatochromic" effect) when different solutes are added to the dye solution. The results for other dyes appear to follow the same pattern, but the values of the $\frac{y}{x}$ ratio in most cases are uncertain because of the difficulty in identifying one of the peaks.

Mechanism of Solute Acion

In the light of the present results different hypotheses to account for the accelerated dyeing of wool in presence of solutes in dyebath are discussed below. It is, however, possible that more than one factor may be responsible for the observed effect and consequently all these hypotheses may be valid to a certain extent.

1. Disaggregation: Disaggregation has been detected in the dye solutions in presence of benzyl alcohol, which is in fact a very effective disaggregating agent for the compounds used here, and therefore, it may be supposed that disaggregation may play some part in the mechanism. However, if it is operative, it must be of comparatively small importance because dioxan also disaggregates dyes, in fact to a greater extent than benzyl alcohol, though it is ineffective in accelerating the rate of dyeing. It has also been shown[84] that when dyeing is carried /...

carried out in presence of large amounts of solvents the rate of dyeing and the equilibrium value are decreased and hence the disaggregation of dyes in solution cannot be the sole reason for observed accelerated effect.

2. Solvent-layer Formation: The three new solutes used here are not suitable to test this theory. It is, however, stated[84] that the formation of a solvent layer would decrease the rate of dyeing and the equilibrium value. The argument is based on the assumption that the rate-limiting step is the diffusion of the dye away from the surface of the fibre towards the centre and that the surface of the fibre is essentially in equilibrium with the bath surrounding it. Thus the rate of dyeing will be related to the activity and not the concentration of the dye in the liquid phase in contact with the solid fibre surface. When a solvent layer is present in which the dye is much more soluble, the activity of the dye in the solvent layer must be much reduced, since it is now in equilibrium with an aqueous phase having a much reduced dye concentration. The fibre surface is essentially in equilibrium with the solvent layer, and thus its activity must also be lower. It, therefore, follows that the rate of dyeing must be lower and that any solvent layer which forms a more concentrated dye layer must show a substantially decreased dyeing rate.

3. Changes in the Fibre Molecules: This appears to be a most likely explanation. Benzyl alcohol is strongly adsorbed by proteins (Fig. 13) and it is probably hydrogen-bonded through its hydroxy group to the substrate /...

substrate molecules, which will mainly be peptide groups, and consequently the benzene nuclei will be presented to the incoming dye molecules. Thus the wool will acquire a hydrophobic surface with diminished polar and other non-ionic forces between the dye and the substrate, and these will reduce drag and allow more rapid passage of the dye molecules down the pores. Inositol will also probably be strongly adsorbed, but its adsorbed layer will present a highly polar surface to the dye solution and this will have a retarding effect on the rate of dyeing probably equal to that of the original polar surface, and consequently inositol is ineffective. Glucose is expected to be adsorbed at basic groups in proteins, but is ineffective for similar reasons to those given for inositol.

4. Removal of Impurities from Wool: This effect has been demonstrated by Medley and Andrews[86] but it cannot be of very great importance because in the present work a similar accelerating effect has also been shown on gelatin and nylon, which do not contain impurities. Both these substrates, however, will be influenced by the solvent adsorption mechanism as stated above.

Action of Solvents in Leather Dyeing

It has been shown recently by El-Mariah and Nursten[107] that the accelerated rate of dyeing in presence of a solvent, observed with wool, is not observed in dyeing chrome leather. There can be two explanations for this as follows: (i) one of the theories of the mechanism of chrome tannage in leather describes the coordination of anionic /...

anionic and non-anionic compounds to the peptide groups in leather. This would block these groups which then would not be available for adsorption of solvent; and (ii) dyeing occurs mainly on the surface of the leather and even if the solvent is adsorbed inside the skin, it will play no effective part in accelerating the rate of dyeing. In either case the suggestion is in agreement with the theory we have just outlined.

PART III

MEASUREMENT OF EXTERNAL SURFACE AREA OF FIBRES

Introduction

The measurement of the specific surface area of finely divided solids is of considerable importance in various industries, e.g., coal, cement, paint, pigment, etc. In the textile industry also the measurement of surface area of fibres is of importance, but since the textile fibres are porous and complex in structure surface area measurements raise complex problems. In such materials, the surface area can be considered of two types, (i) external surface area, i.e., the area of the outside surface of the fibre, and (ii) total surface area, which includes the external area and the total area inside the porous structure. The measurement of the external surface area is of importance when the damage to the fibre surface is to be assessed quantitatively, and this work has not received much attention, perhaps because of the other methods to detect the damage to the fibre surface. The total surface area of the fibres has been measured by some workers[5,108,109], the adsorption of a solute from a solvent being the most commonly employed method, but the results by different workers range from 0.096 x 10^5 $cm.^2$ per gram to about 70 x 10^5 $cm.^2$ per gram on wool and in general are not in agreement. This is probably due to the complex structure of fibres and their property of swelling in certain media and also due to their porous structure whereby molecules of different sizes have different degrees of accessibility to the fibre structure. The present work is an account of investigations carried out to modify and apply solution adsorption technique to measure the external /...

external surface area of fibres and also to see if the same technique could detect and assess damage to the fibre surface.

Various methods have been proposed for the measurement of specific surface, and though most of them are mainly used for powders, pigments, etc., they also could be applied to textile fibres by making proper corrections in some cases, which take into account the difference in the shape, size and the chemical nature of fibres as compared to particles. The different methods are based on the general principle of measuring a factor or a number of factors which are proportional to the surface area and evaluating surface area from these observations. The important methods for measuring the surface area are: (1) adsorption of gases; (2) adsorption of solutes from solution; (3) X-ray diffraction; (4) air permeability measurement; (5) rate of solution of a powder in a solvent; (6) the silvering method and (7) the use of optical or electron microscopy. The general principles on which these methods are based are described below, and their suitability for measurements on textile fibres or otherwise discussed.

(1) The Gas Adsorption Method: This method is based on the evaluation of a quantity known as the "monolayer capacity" of the material under study. This is the quantity of gas which is required to be adsorbed to form a complete layer of single molecules on the surface of the material. This is usually done by bringing the gas in contact with solid material and the amount of gas adsorbed at various pressures is measured. The isotherm thus obtained is made use of in finding out the monolayer /...

monolayer capacity of the material under study and from this value and the size of the gas molecule, the surface area of the material is calculated. Popular adsorbates are nitrogen or a rare gas, at liquid air temperature, or benzene or carbon tetrachloride at or near room temperature. It is very important that the adsorbate must be inert and should not react with or dissolve in the solid, otherwise very misleading results may be obtained.

This method can be applied to textile fibres for surface area measurements, but it suffers from one disadvantage, namely, the fibres to be used must necessarily be dry, and the properties of dry shrunken fibres are likely to be different from those of wet swollen fibres. The method requires complex apparatus and since the molecules adsorbed are relatively small in size, it determines not only the external but the internal surface of the fibres as well.

(2) Adsorption of a Solute from Solution: The principle of this method is the same as that of the gas adsorption method; and it is used for measurement of surface areas of a variety of powders. In this method the solute is dissolved in a suitable solvent and brought into contact with the material under study at different concentrations of the solution. The amount of solute adsorbed on the material at different concentrations is measured and an adsorption isotherm obtained, which is used to calculate the monolayer capacity and thus the surface area. Dyestuffs[110], long-chain[111] fatty acids and many other solutes have been suggested as adsorbates, together with aqueous and non-aqueous solvents. /...

solvents.

The method is not very widely applied to textile fibres, and if water is the solvent, the area obtained is the total area[5,109]. An attempt is made to apply this method to textile fibres in the present work to obtain the external surface areas.

(3) X-Ray Diffraction Method: In this method monochromatic X-rays are passed through a thin layer of the solid under examination and the scattered radiation is collected on a photographic plate. In addition to the intense black spot in the centre, where the undiffracted radiation hits the plate, there is a diffuse surrounding black patch, and from the intensity distribution of this patch the average particle size can be calculated. It is stated[14] that surface area determinations by this method are in good agreement with the results from the gas adsorption method. The method involves very complicated apparatus and the interpretation of results involves highly specialised techniques and hence it is unsuitable as a routine test method. It has not, so far, been applied for the measurements of surface area of fibres.

(4) Air-permeability Measurements: When a current of air is passed through a uniformly arranged mass of fine grained solid, or fibres, packed in a chamber with perforated ends, the ratio of air flow to differential pressure is uniquely determined by the external surface area of the fibres and various constants. This is because the air has to pass through a series of fine channels which is equivalent to flow through a capillary tube, and its flow is determined by the length and /...

and the radius of the tube, and so, indirectly by the surface area of its walls. In this method air is passed under pressure through a bed of solid or fibres and the drop in pressure across the bed is noted, or else the air can be sucked through the material under study, and the difference in pressure against atmospheric pressure noted. The surface area is then calculated from Kozeny's equation[112], which can be written in the form -

$$S^2 = \frac{\Delta p \ (\rho AL - m)^3}{Qk\mu\rho m^2 L^2}$$

where Δp is the pressure difference between the ends of the fibre plug, Q the volume rate of flow through plug, k the proportionality constant depending on the shape of the voids and fibres and on their orientation with respect to the direction of air flow, μ the coefficient of viscosity of air, ρ the density of fibres, m the total mass of plug, L the length of plug, A the area of cross-section of plug and S the surface area of fibres.

The method is suitable for measuring external surface areas of fibres and is simple in operation, but it does not detect the chemical modification of the fibre surface because it is mainly dependent on physical variables rather than chemical ones. Many workers[113,114,115] have used this method and have found it very reproducible and satisfactory. This method is also used in the present work to compare values obtained by microscopic and solution adsorption methods.

(5) Rate of Solution of a Powder in a Solvent: This method depends for /...

for success upon the provision of a solvent which has a uniform reaction, at a reasonable rate and capable of easy and accurate measurement. If W_1 is the weight of a sample of surface area S_1 dissolved in a certain solvent in a certain time, and W_2 is the weight of a sample of the same substance, but with different surface area S_2 dissolved in the same solvent under identical conditions, then weights and areas are related by the equation -

$$\frac{W_1}{S_1} = \frac{W_2}{S_2}$$

If S_1 or S_2 is known the unknown surface area can be calculated. The method has not so far been applied to textile fibres, but if it were it could involve difficulties and drawbacks, e.g., (i) a suitable solvent may be difficult to find, (ii) the absolute surface area value of the same type of fibre must be obtained by some other method, (iii) results of only one type of fibre can be compared, which are again influenced by the surface area value of the standard obtained by other methods, and different types of fibres could not be compared for surface area values, since no single solvent can be suitable for all the fibres.

(6) Silvering Method: This was developed by Clark[116] and is mainly used for paper pulp. It consists of depositing a continuous film of metallic silver (c.a. 0.1μ thickness) on the surface of the pulp and fibrils by virtue of their reducing properties, and then measuring the unknown area of the exposed silver quantitatively by its ability to catalytically decompose a dilute solution of hydrogen peroxide under standardised /...

standardised conditions, as against the effect of measurable surfaces such as silvered cellophane.

This method, since it depends upon the reducing ability of the material under study, can only be used to compare surface areas of the same material treated under different conditions, and hence could not be used to compare the surface area values of different types of textile fibres with one another because their reducing ability will be different depending upon their chemical nature and indeed reducing power is absent in some fibres.

(7) The Microscope Method: A method for estimating the surface areas of irregularly shaped particles by microscope was suggested by Kenrick[117]. The usual method is to project the images of material under study on a screen and evaluate the area from different measurements. In case of irregular particles and those of different sizes, a number of such measurements are made and the average particle surface area, which is related to projected area, is obtained by the equation -

$$\text{average particle surface} = \frac{4\Sigma A}{n}$$

where ΣA represents the summation of areas of the projected images of n particles mounted in random orientation. Various types of microscopes and various optical attachments are in use for a variety of sizes of particles.

This method can be used for textile fibres to measure the external surface area, this being usually done by measuring the fibre diameter with /...

with the aid of a microscope, and considering the fibre as a cylinder, when the external surface area of a single fibre is given by the equation -

$$\text{Surface area} = 2\pi Rh$$

where R is the fibre radius and h is the height of the fibre. Measuring the height and the weight of a single fibre, thus gives the external area of fibres per gram.

In addition to the above mentioned methods for surface area measurements, different methods e.g., heat of wetting[118], electrolytic processes[119], interference[120], radio-tracer[121], tinting strength[122] have been used, but as regards the present problem of measuring the external surface area of fibres they are not of much use.

As stated before, it was also the aim of the present investigations to discover if the solution adsorption method could also be applied to detect damage to the fibre surface, particularly in wool; this would be of considerable interest to wool processors. A glance at the current methods to detect such damage shows that all the methods can be classified as Physical or Chemical, and they are mainly used for wool fibres. The more important ones are described below -

(i) Physical Methods

(a) Visual Examination: Direct visual examination of fibres necessitates the use of the microscope and the method has long been in use. It mainly detects physical modifications on the fibre surface and is qualitative in nature. Advance in technology has been responsible /...

responsible for introducing various modifications in the technique such as, the preparation of surface replicas, half-embedding of the fibre in a medium of similar refractive index, phase contrast microscopy, interference microscopy and electron microscopy of replicas.

(b) Determination of Load/Extension Characteristics of Fibres: The behaviour of fibres when a load is applied to them, and when the load is removed, has long been of practical and academic interest. Studies of the changes in the elastic properties of fibres in various media, before and after particular chemical treatments, provide useful information and facilitate the elucidation of the molecular structure of fibres and of the changes produced by particular treatments.

(c) Swelling Characteristics: The swelling, of wool fibres, in water is mainly controlled by disulphide cross-linkages between protein chains and damage to these cross-linkages increases swelling. The test involves treating the fibres with water and removing the inter-fibre water by centrifuge, then finding out the amount of water retained by the fibres. The method is also applicable to other types of fibres.

(ii) Chemical Methods

(a) Staining Tests: The qualitative detection of chemical modifications to fibres is possible by using tests which make use of the staining properties of the fibres. Most of these tests are empirical but a few depend on specific mechanisms and hence detect specific modifications. The examination of the fibres is usually made by microscope, the damage being judged by the intensity and degree of penetration /...

penetration of the stains.

(b) Allwörden Reaction and K.M.V. Test: These tests are for wool fibres. In the Allwörden reaction the characteristic swelling of the epicuticle of wool fibres in presence of bromine water is made use of. Unmodified wool fibres with undamaged epicuticle are inflated in presence of the reagent, showing blisters on the fibre surface (under a microscope), while modified fibres show this to a lesser extent or not at all.

The K.M.V. test detects acid modification in wool fibres. In presence of the Krais-Viertel reagent (ammoniacal solution of potassium hydroxide) acid-modified wool fibres instantly show a characteristic swelling or lumps under a microsoope. Unmodified wool fibres take a long time (c.a. 6 min.) to show any lumps.

Both these tests are qualitative and can be used in routine work.

(c) Solubility Tests: These depend upon the rate of solubility of fibres in various reagents, the damaged fibres having higher rates. For wool the test usually consists in treating fibres with a reagent under standard conditions and noting the loss in weight. The reagents generally employed are sodium hydroxide, sodium carbonate, urea-bisulphite, hydrochloric acid or alkaline thioglycollate solution.

For cellulosic fibres the method consists of dissolving fibres in a reagent of standard quality and measuring the viscosity of the solution after fibre dissolution. The change in viscosity of this solution indicates the damage quantitatively. The reagent most commonly /...

commonly used is cuprammonium hydroxide, though cupriethylene diamine has positive advantages but is little used.

In addition to the above methods, chromatographic techniques, changes in sulphur and nitrogen content (in wool fibres), etc., have been employed, but are not in common use.

Experimental

In the present work three different methods were used to calculate the external surface area of fibres, to compare with the results obtained by the solution adsorption method. The experimental procedure for each method is described below.

(1) Microscopic Method

To measure the surface area of fibres by this method, the fibre was mounted on the microscope with a projection screen ("Megascope" made by Hans Klöti, Zürich) and the diameter of the fibre was measured. The magnification factor of the fibre image was 500 x and this provided magnification high enough to measure the fibre diameter within the limit of 1μ. In the case of wool fibres, where the diameter is not uniform in a mass of fibres or even along one single fibre, an average of 100 readings was taken, while in the case of nylon, Terylene, and cuprammonium rayon fibres, an average of 50 readings was taken. The average fibre diameter, the standard deviation, and the surface area values of different fibres are summarised in the table below -

Fibre	Diameter (μ)	Standard deviation (μ)	External surface area ($cm^2/gm.$)
Nylon	22.02	1.01	1593
Terylene	20.85	2.09	1389
Cuprammonium Rayon	12.48	1.265	2372
Wool A	23.84	4.298	1271
Wool B	23.82	4.19	1272
Wool C	24.48	5.153	1238
Wool D	26.68	6.177	1136

The /...

The standard deviation (σ) was calculated from the equation:

$$\sigma = \sqrt{\frac{\sum d^2}{k}}$$

where $\sum d$ is the summation of the diameter readings and k the total number of readings taken.

Weights of individual fibres were measured on a "Shirley" Cantilever Microbalance (made for Shirley Developments Ltd., by J. Casartelli & Son, Salford, England). This balance provides high sensitivity and can weigh accurately to 10^{-8} gm. Each individual fibre was weighed twice and an average weight of 10 fibres i.e., total number of 20 weights was taken as the average fibre weight. Knowing the fibre diameter, fibre weight and fibre density the surface area per gram was calculated.

(2) Air-permeability Method

The air-permeability apparatus used in the present work was made according to the air-flow apparatus specifications issued by The International Wool Secretariat, a method approved by The Technical Committee of the International Wool Textile Organization. The apparatus is shown in Fig. 27. The essential parts are a sample holder, air-flow gauge and the manometer.

The sample holder consists of three parts, the base on to which the fibres are placed, the plunger which compresses the fibres, and the screw cap which clamps the plunger to the base. The base and the end part of the plunger have perforations of 0.15 cm. diameter, spaced closely together. The sample holder has an internal diameter of 2.525 cm. and /...

and when the plunger is placed in the sample holder it maintains a gap of 1.7 cm. into which the fibre sample is mounted. The area of cross-section of the plug, that is the space where the fibre sample is mounted, was 5.006 sq. cm.

The air-flow gauge was of the normal type with floating head. It directly measured the amount of air in litres passing through at 15°C. and 760 mm. pressure of mercury.

The manometer was an ordinary glass tube of uniform diameter connected at one end to the lower part of the base and open at the other end. The liquid used in the manometer was distilled water.

The vacuum pump was connected to the air-flow gauge, which in turn was connected to the lower part of the base. When the vacuum pump was started it took air from the air-flow gauge which in turn drew air through the sample holder, and air thus passed through the fibre sample. The difference in pressure between the atmosphere and the air flowing through the fibre sample was indicated by the manometer. The amount of air flowing through the sample was measured on the air-flow gauge and was regulated by having a flow control valve on the rubber tube which connects the vacuum pump to the air-flow gauge.

Since the samples were in the form of either fabric or yarn, they were cut to a very small size so that the twist of the yarn is no longer effective, thus giving loose fibres. The area of fibres was estimated to have increased (by this cutting procedure) by about 1% of the total external area.

All /...

All the experiments were conducted using air at about 65% relative humidity (R.H.) and 20°C, at which the viscosity of air is 1.8×10^{-4} poises. The fibre samples were also conditioned under these conditions for a period of about ten days.

Before starting the experiment the apparatus was tested for its level, which is usually done by noting the level of water in the manometer tube. (If the level in both the arms of the manometer does not coincide with the "zero" mark the apparatus needs levelling.) The fibre sample (2 gm. in present tests) was then weighed carefully and transferred to the sample holder. It was ensured, by fluffing out the fibres with the fingers, that fibres had no hard tangled parts. The sample was inserted gradually in the sample holder and was packed with the fingers to give a uniform packing of fibre in the holder. The perforated plunger was then slowly introduced into the holder and was locked firmly in place with the screw cap. The vacuum pump was then started and the air was slowly drawn in through the holder by opening the flow control valve till the desired air-flow was obtained - as recorded by the air-flow gauge. The difference in pressure in the manometer was noted and the flow control valve was then closed. The sample was removed from the sample holder and the fibres fluffed out between the fingers again and repacked to take a duplicate reading.

In the present tests, all the experiments were done twice at one particular air-flow rate and the whole procedure was repeated at a different value of air-flow. The results, hence represent an average of /...

of four determinations, and it was calculated that the difference in the surface area values was about 1%. This suggests a high degree of reproducibility obtained by this method.

(3) Vapour Phase Adsorption Method

The apparatus used in the present work and the details of its working are described in Part I of this thesis. The general principle of its working is given here. The fibre sample (0.25-0.3 gm.) was mounted on a glass spring in a chamber which was subjected to vacuum of about 10^{-3} mm. of mercury and then the vapours of the solvent were brought into contact with the fibres. The solvent vapours in the chamber, in this work, were maintained at a saturated vapour pressure and at room temperature (c.a. 20°C.). The adsorption of solvent vapours by fibres results in an increase in weight and this is usually measured from the increase in length of the glass spring by a cathethometer. The experiments were all continued for as long as 70 hours (in some cases up to 250 hours) but adsorption was not detected.

(4) Solution Adsorption Method

Usually six dry test-tubes (of ground glass stoppers) were employed. In each of them the yarn or fabric was accurately weighed. The usual amount of fibres taken varied from 0.1-0.2 gm. The necessary range of solutions of different concentrations were made up in ground glass stopper graduated flasks and the required amount of solution (usually 10 c.c., thus giving a liquor ratio of 1:50 or 1:100) was measured out by pipette and run into the test-tube. The time taken for the solution to run into /...

into the test-tube was about 17-20 seconds, and the stop-watch was started after the solution was transferred to the test-tube. The test-tube was then securely stoppered and placed into a mechanical agitator at room temperature. This agitating device has been described by Clunie and Giles[123], and it gives an end-over-end agitation at about 35 revolutions per minute. It was found convenient to put the solution in the test-tubes at intervals of three minutes so that in the meantime the pipette could be rinsed and kept ready for the next solution. After agitating for the determined length of time test-tube was taken out of the agitator and the supernatent liquor was transferred into another clean dry test-tube. The test-tube was usually taken out of the agitator about 15 seconds before the time of the experiment and allowed to stand for 10 seconds before the supernatent liquor was taken out. The experiments were done at room temperature, but only when room temperature was about 20°C.

Method of Analysis

The solutions were analysed by spectrophotometer to obtain optical density values and hence concentration. In most cases the concentrations employed were such that the solutions were dilute enough to read on a spectrophotometer, without diluting any further, using a cell of suitable thickness. In the case of colourless solutions the concentrations were determined by measuring the optical density at maximum absorption wave-length in the ultra-violet region by the Unicam S.P. 500 Spectrophotometer. In the case of coloured solutions the optical density /...

density at maximum absorption wave-length was measured in the visible region on the Unicam S.P. 600 Spectrophotometer. The same measurements were also made on the original solutions, and from the concentration of the original solution before and after the adsorption procedure, the amount of the solute taken up by the fibre was calculated, and an isotherm was obtained. Such experiments were done for three different lengths of time and three isotherms were obtained.

Calculation of the Surface Area

From each of the above mentioned isotherms the monolayer capacity was found from the first plateau of the isotherm, or from "Point B"[14], and from this the surface area for each isotherm was calculated. The surface area thus obtained was plotted against the time for that particular isotherm and extrapolated to zero time to obtain the surface area at zero time.

Calculation of the External Surface Area

The surface area is given by the following equation -

$$S.A. = XmNA$$

where Xm is the monolayer capacity in moles per gram or in these results, moles per gram at the plateau, N the Avagradro number (6.019×10^{23}) and A the area of surface occupied by each solute molecule (in sq. cm.).

Calculation of the Area of Solute Molecule

In the present work, the surface area calculations are based on the area effectively covered by the solute molecule. For adsorption of p-nitrophenol and phenol from a non-polar solvent the orientation of the solute /...

solute molecule on the substrate is taken as end-on (see discussion), while in case of dyes from aqueous solvent it is taken as flat (see discussion). The cross-sectional area of the solute molecules were determined from "Catalin" models. For end-on orientation p-nitrophenol and phenol gave a value of about 15$\mathring{A}^2$ while the dye Rhodamine B gave a value of about 230$\mathring{A}^2$ and Rhodamine 6 GB 215$\mathring{A}^2$.

Substrates

Nylon: Yarn of average fibre diameter 22.02μ was used without any pretreatment.

Terylene: This was also in yarn form having an average fibre diameter 20.85μ and was used without any pretreatment.

Cuprammonium Rayon: This was in fabric form having an average fibre diameter 12.48μ, and was used without any pretreatment.

The samples of wool A-D were supplied by Stevensons (Dyers) Ltd., of Ambergate and had been given the following treatments.

Wool A: This was scoured fabric, the scouring treatment being given in water containing a little Tergitol TMN, and air dried. Average fibre diameter was found to be 23.84μ.

Wool B: This was a wool fabric treated with 2.5% X Acid (unspecified acid, probably due to secret formula) and 2% Sandozol N, treatment lasting for 35 minutes, rinsed and air dried. Average fibre diameter was found to be 23.82μ.

Wool C: This was given a similar treatment as Wool B and then the adsorbed acid was neutralised by treating the fabric with 25% sodium /...

sodium sulphite for 30 minutes, the samples were then rinsed and dried. Average fibre diameter was found to be 24.48μ.

Wool D: This was given ZB finish using the following formula -

3% chlorine

3% Potassium permanganate

10% Calcium chlorite

$\frac{1}{2}$ c.c./lit. V.L.

at an uncorrected pH 10 and 20°C. This treatment was given for 35 minutes and it was then cleared in 5 c.c./litre bisulphite and 2 c.c./litre formic acid. The samples were rinsed and air dried. Average fibre diameter was found to be 26.68μ.

These wool samples were subjected to the Brentamine test and it was observed that the treatments were level.

All the yarns and fabrics were cut to suitable size before adsorption experiments so that effective agitation could be carried out.

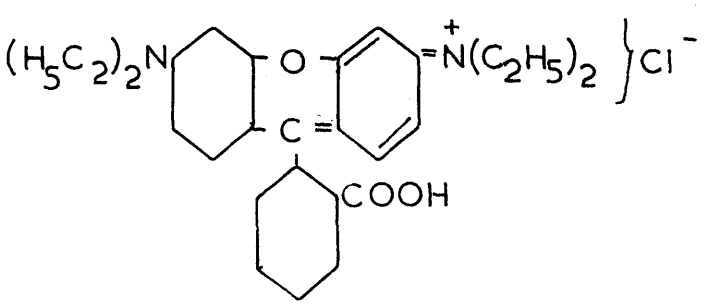
Paper samples 1, 2 and 3 were supplied by T. B. Ford Ltd., High Wycombe. They were beaten for different lengths of time.

Solutes

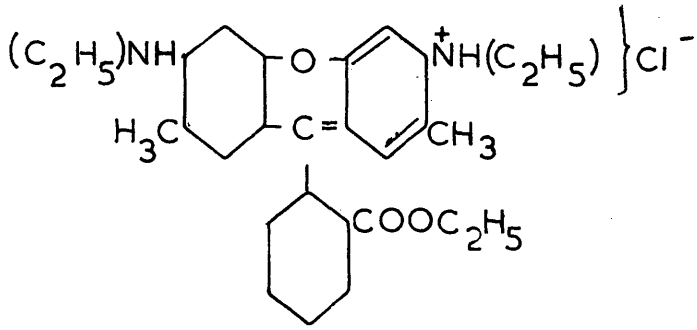
p-nitrophenol: This was recrystallised from water.

Phenol: "Analar" quality Phenol of B.D.H. was used.

Rhodamine B (C.I. 45170): Purified in water-ethanol mixture and purity found to be 95%



Rhodamine 6 GB (C.I. 45160): This was a batch sample supplied by I.C.I. Purity of about 90-92%.



Solvents

The solvents n-hexane, n-heptane, xylene, toluene, iso-octane, cyclo-hexane, n-butanol and 1:4 dioxan were of commercial quality, while with dyes Rhodamine B and Rhodamine 6GB distilled water was used.

Results and Discussion

Since the measurement of external surface areas of fibres is very important particularly in the wool and the paper industries, it is very necessary to have a simple and reproducible method for measuring external surface areas. Some of the methods described above (e.g., microscope, air-permeability, silvering) do make it possible to calculate the external surface area of porous materials, but they do not show the damage due to chemical modifications at the fibre surface, except perhaps the silvering method. The silvering method can only be satisfactory if the area of one particular type of fibre is to be compared with modified fibres of the same type, provided the fibres have suitable reducing groups. Since there is no one chemical method by which the external surface area of different types of fibres can be measured, at the same time yielding information about damage to the fibre surface, it was thought necessary to look into the problem with the hope of developing a new method. Since the method was required to detect minute physical or chemical damage of the fibres, it must necessarily be a sensitive method; and the method which seemed best was solution adsorption. This method has been successfully applied to measure the surface area of various powders, and it was observed by Giles and Nakhwa[17] that p-nitrophenol (PNP) is a very satisfactory solute for most powders, in aqueous and in non-aqueous media. The main advantages of this solute are, (i) its polar nature, ensuring strong attachment to polar surfaces; (ii) its partly hydrophobic character ensuring adsorption by non-polar surfaces; /...

surfaces; (iii) its small molecular size, its planar molecule and its characteristic of adsorbing end-on to the surface, which ensure accurate estimates of the area covered per molecule; (iv) its solubility both in water and in non-polar solvents.

PNP has therefore been used as a solute in the present investigations and the solvents used are non-polar, because if water is used as a solvent the fibres will swell, thus modifying the surface characteristics and giving misleading results. It was observed that if the adsorption is allowed to proceed to equilibrium, PNP penetrates inside the fibre structure from non-polar solvents, hence the surface area values obtained will be for the total surface rather than the external surface area alone. Hence a modification of the normal adsorption technique was followed whereby adsorption was carried out for much shorter times, instead of to equilibrium, and the isotherms were measured after different lengths of time. Since the isotherms thus obtained cannot be called equilibrium isotherms, they are here called "short-period isotherms". A set of short-period isotherms at different times is obtained (usually at three different times) and from the first plateau or from "Point B"[14] of each of these isotherms the surface area of the fibres is calculated. Assuming that the PNP molecule will be adsorbed almost instantly on the fibre surface from a very dilute solution, and then will proceed to diffuse inside the fibre, the surface areas obtained from different short-period isotherms are plotted against time and this gives a straight line. This straight line when extrapolated back to zero time gives the external /...

external specific surface area of the fibre, and in the present work this is assumed to be a true external surface area value. It must, however, be stressed that the surface area thus obtained may not be an absolute value, because the fibre surface, being rough, is expected to give a higher value compared with other methods, e.g., the microscopic method, because as a small molecule such as PNP is expected to be adsorbed in small rough portions and crevices on the fibre surface which the microscopic method may not be able to measure. How much this area is will vary with different fibres, but as an approximation, after studying the photomicrographs of wool and nylon, the author is of the opinion that this area is likely to be 10-20% higher than the area observed by the microscope. However, it is safe to conclude that the surface areas measured by the method will be "apparent external surface areas" and in direct relation to the true area, since the results of the present investigations are reproducible and comparable to results from the microscopic and air-permeability methods. The fact that the results by these three methods are comparable with each other justifies the assumption that PNP molecules are adsorbed instantly on the external fibre surface.

Shape of the Isotherms (Short-period) and Effect of Moisture

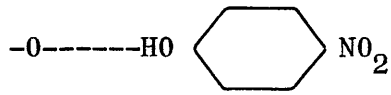
By the classification system of isotherm shapes suggested by Giles et al.[15,16], the short-period isotherms in the present work are mostly of L type (Figs. 28,29). However, in the case of adsorption of PNP on cuprammonium rayon and Terylene (Fig. 30B,C) and of phenol on nylon /...

nylon (Fig. 31B) an isotherm of S type was observed. This was thought to be due to the presence of moisture in either the solvent or the solute, or the substrate, which water competes with the solute for the polar surface of the fibres and so retards the adsorption of solute in the initial stages of the adsorption process. This was confirmed by intensively drying all glassware, and the solvent, solute and substrate, in the adsorption of phenol on nylon from n-heptane. The solvent was dried by keeping it in contact with sodium wire over a few days. The phenol was dried by keeping it under vacuum for a period of over 7 days and the nylon was dried in an oven at 70°C overnight. The adsorption isotherm (short-period) then obtained was of L type (Fig. 31A) confirming the hypothesis that the presence of moisture was responsible for the unexpected S isotherm. The value of adsorption, after drying, was, however, much lower as compared to the adsorption obtained before drying, suggesting that complete absence of moisture retards adsorption in some way and that traces of moisture act as a kind of catalyst in the adsorption process. A similar effect has also been observed by the author's colleague, I.A. Easton, who found a change in the shape of the isotherm with lower adsorption value, in his studies on adsorption of phenol on chitin. Similar effects have also been observed by other workers[124,125]. An attempt was made to find out if this result could also be confirmed with PNP on Terylene and cuprammonium rayon from n-hexane, but it was observed that when PNP and n-hexane were intensively dried, the solubility of PNP was so low that it was very difficult to obtain /...

obtain an isotherm. However, there is enough evidence to suggest that the presence of moisture sometimes alters the shape of an isotherm from L to S, the moisture most probably competing with the solute for active adsorption sites on the substrate.

Orientation of Solute Molecules

PNP is normally adsorbed end-on on polar surfaces from polar solvents, probably by hydrogen bonding between -O atoms on the substrate and the OH groups in the PNP molecule, thus -



and hence as stated previously it gives an S isotherm. From non-polar solvents it gives an L type of isotherm but still it is believed to be adsorbed end-on[109]. The reason is that the non-polar solvents have no affinity for the polar substrates and hence do not offer any kind of competition to the PNP molecule. Moreover, the fibres are not swollen by non-polar solvents and the size of the solvent molecule being bigger than the pore-size of the fibres, there is little chance of solvent molecules diffusing inside the fibre structure, and very slowly, if at all. From "Catalin" models the area of the PNP molecule in the end-on orientation is found to be 15$\mathring{A}^2$, and this value is used by other workers[17] and is also used in the present work for the surface area calculations. Phenol is also believed to be adsorbed in a similar way as PNP, and gives similar values for cross-sectional area for end-on orientation. It is believed, however, that the true area should be c.a. 25$\mathring{A}^2$ /...

c.a. 25$\mathring{A}^2$ if the separation is the same as in the graphite crystal. We use 15$\mathring{A}^2$, however, because this gives values agreeing closely with the microscopic test. We cannot explain however why 15$\mathring{A}^2$ thus appears correct.

The dyes Rhodamine B and Rhodamine 6 GB were adsorbed from aqueous solutions and since they give L types of isotherm, they are believed to be adsorbed lying flat and their cross-sectional areas as measured from the "Catalin" models are 230$\mathring{A}^2$ and 215$\mathring{A}^2$ respectively.

Results by Microscope Method

The results are summarised in Tables VI and VII. Since the main aim of the present investigations was to investigate the possibility of using solution adsorption methods for the measurement of external surface areas of fibres, it was necessary for the results obtained by this method to be compared with the results from other methods. The microscope method was selected as it is one of the few methods which measures the true external surface area of fibres. Since the fibre is not exactly circular in cross-section, when mounted on the microscope slide it tends to lie flat on the slide and will give slightly higher values of diameter and so higher surface area results. Moreover this method will detect the roughness of the fibre surface only in proportion to the magnification of the image employed, and hence the surface area results are dependent on the magnification employed.

Results by Air-permeability Method

This method has been used extensively for surface area measurements of /...

of powders but is not very often applied for textile fibres. Lord[113] has tested the method on different fibres and observed that as required by Kozeny's[112] equation the rate of flow was proportional to the pressure difference and pressure head, and inversely proportional to the sample length and square of the specific fibre surface, it was not proportional to the porosity function. This was determined by calculating the values of constant k at different air-flow and it was observed that increase in porosity value leads to an increase in the value of constant k and when porosity values are nearing unity, the value of constant k rises very rapidly. Similar observations have been made by other workers[126,127]. Consequently the value of the "constant" in Kozeny's equation -

$$S^2 = \frac{\Delta p(\rho AL - m)^3}{Qk\mu\rho m^2 L^2}$$

varies with the porosity. The value of this constant k has been calculated by Lord[113] from the various experiments and tabulated for different fibres and different masses of the plug (related to porosity) used in his experiment. He has also tabulated Emersleben's[126] data, giving the value of this constant for different porosity values. The usual method for determining the value of this constant is to take fibres of known surface area, usually determined by the microscope method, and measure other variables to substitute their values in the equation before calculating the value of constant k. Thus the air-permeability method is dependent on other methods for calibration purposes. In the present work it was not possible to calibrate the air-permeability apparatus /...

apparatus to determine the constant k for different fibres, because this method was itself used to check surface area values obtained by the microscope. Thus the constant k had to be taken from other data, and in the present work Emersleben's[126] data has been used because he calculated these values from his studies on parallel circular rods which would resemble ideal fibres, and the value was taken to be 13.6, which corresponded to a porosity value of 0.947, the porosity of the present mass of fibres being of the same order.

The results by this method are tabulated in Tables VI and VII, and their relation to microscope values are shown in Fig. 32. It is seen that the air-permeability results are higher in almost all cases by a small but constant factor, and there may be reasons for this. By examining Kozeny's equation it is seen that if the microscope is used to calculate the surface area for the purpose of evaluating the value of constant k; as the value tends to be high because of the irregular shapes of fibres, the value of k will be lower. This value of k when used in the present data will give high values of surface areas. Secondly, as stated before, the fabric and yarn was cut to very small size, which increases the surface area by about 1.0%. Also since the constant k is dependent on the shape of the voids and fibres and on their orientation with respect to the direction of air-flow, it cannot be the same for all the different fibres, as it is taken to be in the present work. Considering these points, it is thought that the air-permeability results are fairly comparable to those by microscope. The fact that the differences /...

differences between the results by microscope and by air-permeability have a constant factor, and assuming that both the methods should give comparable results, the difference must be due to the value of the constant k used in the present work. This could not be avoided because this value could not be determined due to the difficulty stated above.

Results by Vapour Phase Adsorption Method

This method was used in the hope of measuring external area of fibres by adsorbing vapours of various solvents, e.g., n-hexane, cyclo-hexane, etc., so that an extra method could be made available to check the results by solution adsorption. The apparatus, as mentioned before, was the same as described in Part I of the present thesis. It is known that molecules bigger in size than n-butanol do not diffuse inside the wool fibre[39]. It was thought that if large molecules such as n-hexane or cyclo-hexane are adsorbed on wool fibres, they must be adsorbed on the outer surface, hence making it possible to calculate the external surface area. It was found that even after exposing wool and nylon fibres to the vapours of these solvents for 70 hours, and in some cases for as long as 250 hours, no adsorption was detected by increase in weight of the fibre sample. Though this method did not produce the results expected, it confirmed the assumption made in using a non-polar solvent in solution adsorption, that the solvent is not adsorbed, or very slowly to an extent which could not be measured by this method, by the fibres and that only PNP is adsorbed, initially on the outer surface, subsequently diffusion inside the fibres.

Results /...

Results by Solution Adsorption Method

A similar kind of technique, as used in the present work, has been followed by Beamesderfer et al.[128] by which they have tried to calculate the external surface area of wood pulp. They adsorbed a dye - Benzo Fast Scarlet 4BSA - on wood pulp from water for different lengths of time at various electrolyte concentrations and calculate the surface area of the pulp from these isotherms. They also determined the surface area of the samples by other methods, e.g., silvering and air-permeability, and compared the adsorption results with those obtained by these methods, and the conditions and time in the adsorption method which gave surface area values agreeing with other methods were taken as standard conditions. This method gives an apparent area of the wood pulp surface which will be related to the true surface area value, but it has some serious objections, namely, (i) the surface characteristics of wood pulp will change markedly when it comes in contact with water, so that the area measurements are far different from the original values, (ii) the molecular area measurements of the dye seem to be doubtful. These authors give the molecular area of the dye as 141$\mathring{A}^2$, but it gives a value of about 310$\mathring{A}^2$ by the "Catalin" models, which are used for the present work, (iii) a large molecule of a dye such as Benzo Fast Scarlet 4BSA is very likely to aggregate and unless this is allowed for, it can give very misleading results.

These objections have been avoided in the present work by using non-polar solvents to avoid swelling of fibres, by using PNP, whose molecular /...

molecular area has been established fairly accurately[17], and which does not aggregate in solution. The other advantage of the present method is that the values are checked with those obtained by microscope and by the air-permeability method. In cases where there is no agreement with these values, explanations for the deviations have been given.

Adsorption of PNP: As stated above, this solute was used in non-polar solvents and the results are shown in Figs. 33,34,35 and summarised in Tables VI and VII. In all cases the surface areas obtained from the first plateau or "point B"[14] of the isotherm and values thus obtained from different short-period isotherms at different times are plotted against time and by extrapolating back to zero time the external surface area is obtained. The main assumption here is that PNP is almost instantaneously adsorbed on the outer surface of the substrate. For this assumption to be valid PNP should not have a very high solubility in the solvent, otherwise it will take a long time to be adsorbed on the outside surface of the substrate, because the breaking of solute-solvent bonds will require too much energy and take too long. This is in fact shown by the present results; where PNP has a high solubility in non-polar solvents low surface area values are obtained, while only solvents in which PNP is sparingly soluble give comparable results with other methods. The relation between the logarithm of solubility of PNP in non-polar solvents and the logarithm of surface area values is shown in Fig.36. This straight line relationship shows that the assumption made about PNP adsorbing on the substrate surface completely /...

completely and instantaneously is valid only if the solubility of PNP is low in the solvent. The data plotted appear to show that the relationship is different for solvents with molecules of large cross-section compared with aliphatic ones with small cross-section.

It is seen from Figs.28, 29, 30 that in some cases the first plateau of the short-period isotherms does not continue over a long range of concentration, instead there is an inflection and the isotherm then rises further. Since this inflection is obtained at the same concentration in all the short-period isotherms in one set it is easy to recognise, but still attempts were made to select a solvent in which PNP has low solubility and which gives a clear and long well-defined plateau. It was observed that generally PNP gives a fairly long and well-defined plateau in cases when it is used from a solvent in which it has high solubility or from cyclic solvents while the solvents in which it has low solubility give rather short and abrupt plateaux. An attempt was made to take advantage of the well-defined plateau given by some solvents, which gave low surface area values by virtue of the high solubility of PNP, by mixing them with other solvents, and also by using such solvents only for dissolving PNP (a drop was used in most cases) and then making up the solutions with a solvent which gives a poor plateau, but these tests were not successful. In all cases when mixing of solvents was tried the isotherms gave short plateaux. The aromatic solvent will probably have the higher affinity for the fibre (c.f. benzene + cyclohexane on carbons[129]) and thus will enter the fibre the more slowly /...

slowly (c.f. Part II), thus the liquid inside the fibre has low solubility characteristics and causes the poor plateau effect.

Detection of Modification to Fibre Surface

The surface area measurements on modified samples of wool showed that the present method could be used for detecting modification to the surface of wool fibres. The four samples of wool used were (i) scoured wool, (ii) acid treated wool, (iii) acid treated wool with subsequent neutralisation of acid and (iv) alkali treated wool. The adsorption of PNP was carried out from two solvents, n-hexane and iso-octane; and the results are shown in Figs. 37, 38 and Tables VI and VII. It is observed that the scoured wool gives a surface area value which is comparable to the microscope value, while the alkali treated wool gives a surface area value which is higher than the microscope value. The acid treated wool with the acid subsequently neutralised and the unneutralised acid treated wool give higher surface area values than by the microscope and than alkali treated wool. The order of modification is, acid treated wool > acid treated subsequently neutralised wool > alkali treated wool > scoured wool.

These results throw light on the mechanism of attachment of PNP to wool. It is known[109] that PNP is adsorbed to the substrate by the mechanism of hydrogen bonding and in wool the two likely groups it can bond with are the amino and the carboxyl groups. When wool is treated with acid, the following reaction is believed to occur -

$$R - COO^- / H_3N^+ - R + H^+ \longrightarrow R - COOH + H_3N^+ - R$$

thus /...

thus carboxyl groups where PNP is thought to be hydrogen bonded are freed. The treatment of wool with alkali follows the reaction -

$$R - COO^- / H_3N^+ - R + OH^- \longrightarrow R\text{-}COO^- + H_2N\text{-}R + H_2O$$

in which case PNP can attach itself by being hydrogen bonded to the amino groups. At the same time treatment with both acid and alkali will damage the epicuticular layer of wool fibres. Thus treatment with both acid and alkali will increase the permeability of wool fibres to a great extent and at the same time set carboxyl groups free for hydrogen bonding reactions in the former case and amino groups in the latter case. From the present results it is seen that acid-treated wool gives the highest surface area values as compared with other wool samples, which suggests that the affinity of hydrogen bonding between PNP and carboxyl groups is lower than the heat of hydrogen bonding of PNP and amino groups.

The examination of the surface area results by PNP on modified samples of wool from n-hexane and iso-octane shows that for scoured wool the surface area values from iso-octane is lower than the n-hexane value, but when the values for alkali-treated wool and acid-treated wool are compared it is seen that surface area values from iso-octane increase in a greater proportion than the values from the solvent n-hexane. The relation between the hexane values and iso-octane values is shown in Fig. 39. The interesting feature is the straight line relation and it is difficult to explain why iso-octane should give lower surface area values for scoured wool than n-hexane, and yet give higher surface area values /...

values for acid-treated wool than n-hexane. The only explanation the author can offer at present is that the differences are due to differences in ease of penetrability of the fibre by the solvent, in liquid form (when they penetrate, they allow more PNP to be adsorbed). On this view it would appear that n-hexane penetrates scoured wool better than iso-octane, but that as the fibre damage increases the effect reverses. This might be due to some change in the disposition of the hydrophobic groups in the fibre molecules.

Comparison of Results by Different Methods

From the Table VI it is seen that the solution adsorption method gives comparable results to the microscopic method when the solubility of PNP in the solvents is low, while the results by air-permeability method are all higher than those given by the microscope by a constant factor. In no case does the solution adsorption method give a much higher value than the microscopic results, and hence the latter are taken as true values for the surface areas in the present work. This leads to the conclusion that the solution adsorption method could be applied in the present form to obtain surface area values of a variety of fibres to give values comparable to microscopic values, thus giving a chemical method for the measurements of external surface of fibres. The advantages of the present method over the microscopic method are (i) it can detect damage to the fibre surface; and (ii) it can be less laborious and could be used as a routine test method if proper calibrations are ready, whereas the microscopic method involves a tedious procedure /...

procedure of repeating many readings. The present method, though much more time consuming than the air-permeability method, has an advantage when damage to the fibre surface is to be considered.

Time of Experiments: Since the present technique enables to measure the external fibre surface and also to detect damage to the fibre surface, it can be established as a routine method to evaluate these properties of fibres. For the method to be established as a routine test the total time taken for the experiments is very important, and hence this aspect has been carefully examined. The different procedures involved and the approximate times required are as follows:

(i) Preparation of solutions, 2 hours.

(ii) Weighing of fibres in test-tubes, $1\frac{1}{2}$ hours.

(iii) Adsorption, $\frac{1}{2}$ - $1\frac{1}{2}$ hours, according to nature of fibre.

(iv) Spectrophotometric measurements of solutions before and after adsorption, 2 hours.

(v) Calculation and plotting of isotherms, $\frac{1}{2}$ hour.

Thus in all it takes from 8 to 10 hours to complete a set of experiments. This time can be shortened in various ways if tests are done on a routine basis. For example, stage (i) can be eliminated by having solutions prepared in large quantities; and if only comparative values are required, only one isotherm is needed. This reduces the total time to about 3 to 4 hours. In the present work this time saving technique has not been examined.

Use /...

Use of Basic Dyes

The present method for the measurement of surface area of fibres involves the use of water immiscible solvents. It was thought that if a dye could be used in water, the method could be much simplified. Thus it might be possible to extend the method of Beamesderfer et al.[128] on paper fibres to enable it to be used for textile fibres.

To use a dye successfully in this way, it is very important for its mode of orientation on the substrate to be known. McKay in this laboratory has shown[20] that the basic dye Rhodamine B is adsorbed most probably as a monolayer flatwise on graphite, where the adsorption must be largely due to van der Waals attraction between the non-polar surface and the aromatic ring system of the dye molecules. On highly polar or ionic surfaces, e.g., alumina, this dye was shown to be oriented vertically. The cause is the ion-ion attraction between anionic sites in the substrate and cationic groups in the dye molecule. From this knowledge of the orientation of Rhodamine B dye on different substrates, it was possible by studying equilibrium isotherms on wool and silk to determine its probable orientation on protein fibres. It was observed that on both these substrates the dye was adsorbed in a manner suggesting a flatwise orientation. The probable orientation having been established, it was possible to evaluate the use of the dye for measuring external surface area. A related basic dye, Rhodamine 6 GB, was also used.

The results, shown in Figs. 40, 41, 42, are unfortunately unsatisfactory. /...

unsatisfactory. The apparent external surface areas found are many times greater than those found using an anhydrous solvent, and it is obvious that the fibres are much swollen by the water and the internal area is being measured. Adsorption of dye micelles, rather than single dye cations, by the fibre might also be partly responsible for the higher values.

It was next decided to modify the fibre by treating it first with cetyltrimethylammonium bromide (C.T.A.B.) and thereby to obtain a positively charged surface which might repel the cationic basic dye and so give a lower surface area value. This in fact did not occur, and the surface area value obtained was the same as that given by the untreated wool sample. This may have been due to a complete washing off of the C.T.A.B. in rinsing. Attempts were made to use other coloured solutes, e.g., azobenzene and the water-insoluble dye dimethyl yellow (dimethylaminoazobenzene) on wool from n-butanol, a non-penetrating solvent, but they were not adsorbed at all, no doubt because of preferential adsorption of the highly polar solvent on the external fibre surface.

Surface Area of Paper Pulp

In order to determine whether the present method could be applied to measure the external specific surface of pulp, three samples of paper pulp beaten for different lengths of time were acquired from T.B. Ford Ltd. of High Wycombe. The results by the present method are presented in Figs. 43, 44, 45 and Table VIII. After receiving the present results /...

results this firm supplied the results of the different tests they had done on the same samples. They measured the Drainage Rate and Fibre Length Index.

Drainage Rate[130]: The test is usually employed to determine the degree of beating. The drainage rate (expressed as degrees Schopper Riegler - SR^{o}) is measured by the ease with which water passes through paper-making fibres while they are being formed into a wet mat on the perforated plate of the drainage tester. The time, in seconds, is taken for the drainage of a certain volume of pulp suspension.

The results of the drainage rate depends on temperature, consistency of the stock and the degree of beating of the fibres. Drainage rate increases with increased beating, i.e., increased surface area.

Fibre Length Index[130]: This is a method which gives a measure of the fibre length, the surface area increasing with decrease in fibre length. The principle of the method is that a dilute solution of pulp is passed through fixed blades which form a grid. The fibres retained on the grid are collected, dried and weighed, and the weight in grams is expressed as the fibre length index.

Comparison of Results: With beating of paper pulp the surface area increases and this increase is mainly due to the increase in the fibrillation of the pulp and the reduction in length of the pulp fibre. Hence an increased beating will lead to an increase in drainage rate and a reduction in fibre length index. An examination of the results presented in Table VIII shows that those by the present method do correlate /...

correlate with the corresponding values of drainage rate and fibre length index.

In order to get surface area values from the drainage rate data, the results of Ingmanson and Andrews[131] were used and from their work on wood pulp it was possible to calculate roughly the surface area of wood pulp for the corresponding drainage rates of the paper samples. The results in Table VIII show that surface areas of wood pulp increase in a greater proportion as compared to paper pulp with increased beating. This is to be expected, as wood pulp on beating increases more in surface area as compared to the cotton pulp which is used in the preparation of paper samples used in present work[132].

Isotherms on Paper: When PNP was adsorbed on paper pulp fibres from iso-octane the resulting isotherms were of unusual shape. They are shown in Figs. 43, 44. It is seen that after the inflection point they tend to rise very suddenly and at the same time tend to move towards the ordinate, which means that the equilibrium concentration of the solution is the same at two given points, while the amount adsorbed is different. This tendency is less pronounced in sample 1, while it becomes increasingly marked with the samples of increased beating, and is at a maximum in sample 3. This is believed to be due to the different characteristics of the surface of pulp fibres, as compared to textile fibres, the surface of pulp fibres being highly fibrillated, and the number of fibrils increases with increased beating, resulting in this unusual, indeed previously unknown, shape of isotherm, which becomes /...

becomes more pronounced from paper sample 1 to 3. During the adsorption of PNP, since the surface is fibrillated, it seems to be adsorbed on the surface of the fibrils; and once this surface is fully covered, PNP must be diffusing rapidly inside the surface pores, thus giving a backward shift in the resulting isotherm. If this was true, the surface area of the paper should not be very different at different intervals of time. This is actually found to be the case, when examination of time against surface area plots (Fig. 45) shows that the lines are almost horizontal to the time axis.

A P P E N D I X

Statistical Analysis of Results Presented in Part II:

I: Relation between Number of Carbon Atoms and Washfastness:

To discover if there is any relationship between wash fastness (y) and the number of carbon atoms in a dye molecule (x), a regression analysis was carried out on the data.

Since it was desired to estimate y from x, y is the dependent variable and x the independent variable. The best fitting straight line was calculated by the method of least squares and is given by:

$$Y = \bar{y} + b(x - \bar{x})$$

where Y = predicted value of the dependent variable,

$\bar{y}$ = mean of observed values of dependent variable,

$\bar{x}$ = mean of values of independent variable,

$b = \frac{p}{t}$ = regression coefficient,

$p = \sum y(x - \bar{x})$

$t = \sum (x - \bar{x})^2$

To test if the above line is significant an analysis of variance was carried out thus, (n = number of dyes):

Source of Variance	Degrees of Freedom	Sum of Squares
(i) Due to Regression	$N_1 = 1$	bp
(ii) About Regression	$N_2 = n - 2$	u - bp
(iii) Total	n - 1	$u = \sum (y - \bar{y})^2$

The mean square is calculated by dividing the sum of squares by the degrees of freedom. If the mean square from (i) is significantly greater /...

greater (by the F-test) than the mean square from (ii) then the regression is significant.

Now n = 125, $\Sigma x = 3329.0$, $\Sigma y = 349.5$, $\Sigma xy = 9813.0$, $\Sigma x^2 = 96363.0$, $\Sigma y^2 = 1119.25$

$\therefore b = 0.06555$

$\therefore y = 0.06555x + 1.0503$

To test if the above line is significant an analysis of variance was carried out thus:

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square
(i) Due to Regression	1	33.1072	33.1072
(ii) About Regression	123	108.9408	0.8854
(iii) Total	124	142.0480	

This data gives F = 37.38, with $N_1 = 1$ and $N_2 = 123$. This value is highly significant, therefore straight line is highly significant and ratio of sum of squares (i) and (iii) show that it accounts for 23% of total regression.

II: <u>Relation between Total Number of Atoms and Wash Fastness</u>:

n = 125, $\Sigma x = 7647.0$, $\Sigma y = 349.5$, $\Sigma xy = 22503.0$, $\Sigma x^2 = 507927.0$, $\Sigma y^2 = 1119.25$

$\therefore b = 0.02797$

$\therefore y = 0.02797x + 1.0849$

To test if the above line is significant an analysis of variance was carried out, thus:

Source /...

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square
(i) Due to Regression	1	31.3821	31.3821
(ii) About Regression	123	110.6659	0.8997
(iii) Total	124	142.0480	

This data gives F = 34.88, with $N_1 = 1$ and $N_2 = 123$. This value is highly significant and accounts for 22% of total regression.

III: Relation between Number of Carbon Atoms and Migration Number:

$n = 90$, $\Sigma x = 2373.0$, $\Sigma y = 245.5$, $\Sigma xy = 6038.0$, $\Sigma x^2 = 68575.0$, $\Sigma y^2 = 789.75$

$\therefore b = -0.07242$

$\therefore y = -0.07242x + 4.626$

To test if the above line is significant an analysis of variance was carried out, thus:

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square
(i) Due to Regression	1	31.4867	31.4867
(ii) About Regression	88	88.5939	1.0067
(iii) Total	89	120.0806	

This data gives F = 31.28, with $N_1 = 1$ and $N_2 = 88$. This value is highly significant and accounts for 26% of total regression.

IV: Relation between Total Number of Atoms and Migration Number:

$n = 90$, $\Sigma x = 5382$, $\Sigma y = 245.5$, $\Sigma xy = 13843.5$, $\Sigma x^2 = 349134$, $\Sigma y^2 = 789.75$

$\therefore b = -0.03069$

$\therefore y = -0.03069x + 4.5630.$

To /...

To test if the above line is significant an analysis of variance was carried out, thus:

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square
(i) Due to Regression	1	25.7042	25.7042
(ii) About Regression	88	94.3764	1.0725
(iii) Total	89	120.0806	

This data gives F = 23.97, with N_1 = 1 and N_2 = 88. This value is highly significant and accounts for 21% of total regression.

V: Relation between Wash Fastness and Migration Number:

(A): Taking migration number as a dependent variable (y) and wash fastness as independent variable (x).

n = 85, Σx = 234.0, Σy= 235, Σxy = 594.5, Σx^2 = 726.5, Σy^2 = 762.5.

$\therefore b = -0.6371$

$\therefore y = -0.6371x + 4.5186$

To test if the above line is significant an analysis of variance was carried out, thus:

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square
(i) Due to Regression	1	33.41	33.41
(ii) About Regression	83	79.3841	0.9339
(iii) Total	84	112.7941	

This data gives F = 35.77, with N_1 = 1 and N_2 = 83. This value is highly significant and accounts for 30% of total regression.

(B): Taking wash fastness as a dependent variable (y) and migration number as an independent variable (x).

n =/...

$n = 85,\ \Sigma x = 235.0,\ \Sigma y = 234.0,\ \Sigma xy = 594.5,\ \Sigma x^2 = 762.5,\ \Sigma y^2 = 726.5$

$\therefore b = -0.4649$

$\therefore y = -0.4649x + 4.0383.$

To test if the above line is significant an analysis of variance was carried out, thus:

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square
(i) Due to Regression	1	24.3784	24.3784
(ii) About Regression	83	57.9334	0.6980
(iii) Total	84	82.3118	

This data gives $F = 34.93$, with $N_1 = 1$ and $N_2 = 83$. This value is highly significant and accounts for 30% of total regression.

Table I.

Pore-size Distribution Data for Lincoln Wool

Adsorbate Vapours	Adsorption at Saturation (mm/gm.)	Length of Adsorbate Molecule (Å)	Pore-size Distribution	
			%	Diameter (Å)
Water	13.4	3.1	40.3	3.1 - 4.0
Methyl alcohol	8.0	4.0	23.5	4.0 - 4.5
Ethyl alcohol	4.85	4.5	26.9	4.5 - 6.1
n-Propyl alcohol	1.25	6.1	9.3	6.1 - 7.3
n-Butyl alcohol*	0	7.3	0	>7.3

* Ref. 39.

Table II

Pore-size Distribution Data for Merino Wool

Adsorbate Vapours	Adsorption at Saturation (mm/gm.)	Length of Adsorbate Molecule (Å)	Pore-size Distribution	
			%	Diameter (Å)
Water	14.2	3.1	43.67	3.1 - 4.0
Methyl alcohol	8.0	4.0	25.35	4.0 - 4.5
Ethyl alcohol	4.4	4.5	25.347	4.5 - 6.1
n-Propyl alcohol	0.8	6.1	5.633	6.1 - 7.3
n-Butyl alcohol*	0	7.3	0	>7.3

* Ref. 39.

Table III

Rate Data for Dyes on Gelatin and Wool from Various Solvents

Dye	Solvent*	Gelatin[1]					Wool[1]				
		$t_1^{\frac{1}{2}}$ min	exh_1 %	$t_2^{\frac{1}{2}}$ min	exh_2 %	slope	$t_1^{\frac{1}{2}}$ min	exh_1 %	$t_2^{\frac{1}{2}}$ min	exh_2 %	slope
I	W	2	6	4	20	7.1	2	12.5	4	28.6	8
II	W	2	19	4	49.2	15.1	1.8	19	4.5	59	15
II	WBz						1.6	13.6	4.7	66	16.3
III	W	2	16	4	39.7	12.9	2.1	20.5	4.7	52	12
III	WBz						2	12	5.2	54	13
IV	W	2	10.9	4	29.2	9.2	1.6	10	5	44.5	10.2
IV	WBz						2.3	11.6	5	37.5	9.5
Va	W	2.8	12	4.5	25.5	7.9	2.9	13.8	5	33.7	9.5
Vb	W	2.7	9.3	4.8	24.9	7.4	2.2	8.8	4.3	27.3	8.8
Vc	W	2.9	7	5	19	5.8	2.8	7	5	22	6.8
Vd	W						2.5	36.7	4	41.5	3.3
VIa	W	1.6	10	4.8	51	12.7					
VIb	W	2.6	9.7	5	25	6.5					
VII	W						2	4	4.8	15.5	4.1
VIII	W	2.1	3	4.8	20	6.3	2.5	13.5	4.6	33	9.5
VIII	WBz	2	12	4.6	36.5	9.5	1.9	17	4.3	53	15

cont'd

Table III cont'd.

VIII	WD						2.2	14.5	4.8	40	9.8
VIII	WG						2.7	17	4.8	33.5	7.9
VIII	WI						2.7	17	4.8	33.5	7.9
IX	W	2.9	4.7	5	14	4.4	1.8	6	5	22	5
IX	WBz	2.5	7	4.9	27	8.4	2.2	16	4.4	42	11.8
X	W	2.4	11	4.3	29	9.2					
XI	W	2.3	6	5	20	5.2	3	11.5	4.9	24	6.7
XI	WBz						2.5	22	4	43.5	14.4
				Nylon[/]							
VIII	W	2.5	1.5	4.9	4	1					
VIII	WBz	2.3	2	4.7	10.5	3.6					

---

*W = water alone; WBz = 3% (vol/vol) benzyl alcohol-water; WD = 3% (vol/vol) dioxan-water; WG = 3% (wt/vol) D-glucose-water; WI = 3% (wt/vol) meso-inositol-water.

/$t_1^{\frac{1}{2}}$, exh_1, $t_2^{\frac{1}{2}}$, exh_2, are the respective values of $t^{\frac{1}{2}}$ and corresponding percent exhaustion at the beginning and end of the linear part of the curves.

Table IV

Effect of Basicity of Acid Dyes on some Kinetic Properties on Wool

Dye	Basicity	Relative rate of Dyeing in acid soln. *	Relative rate of Dyeing in acid soln. /	Relative rate of Desorption‡ in alkaline soln.	Diffusion coefficient ($\times 10^8$) at 70°C. in acid soln.
II	1	c.a.4.0	1.19	1.6	1.11
III	2	c.a.0.4		5.2	
IV	3	c.a.0.22	0.82	12.1	0.60
Ponceau 6R (C.I. 16290)	4			16.0	

*1% shades of the commercial dyes (standardised with salt), Naphthalene Red J, Naphthalene Red EA, and Naphthalene Scarlet 4R, dyed in 50-volume baths with 3% sulphuric acid and 10% Glauber's salt, at 60°C (70); expressed here as reciprocals of time (min.) of half-dyeing.

/From Table III and Figures 9 and 11.

‡2% shades of the same dyes, unstandardised, applied at bath pH 3.0, desorbed in 75-volume baths of 0.05 sodium borate at 40°C (72).

Table V

Absorption Data (x- and y- bands) for Dyes in Various Media

Dye	Medium*	λ_{max} y	λ_{max} x	O.D. at λ_{max}. (x) in 1 cm. cell	O.D. ratio, y/x
		Reactive dye			
Procion Brilliant Blue H7G (ICI)	W	6250	6600	0.920	0.71
	WBz	6250	6650	1.230	0.54
	WD	6250(?)	6650	1.470	0.44
	WG	6250	6600	0.850	0.71
	WI	6250	6600	0.850	0.71
		Metal-complex dyes			
VIII	W	4800	5250(?)	0.466(?)	1.57(?)
	WBz	4800	5300(?)	0.487(?)	1.49(?)
	WD	4870	5250(?)	0.520(?)	1.42(?)
	WG	4800	5250(?)	0.430(?)	1.60(?)
	WI	4800	5250(?)	0.420(?)	1.62(?)
X	W	5500	5950(?)	0.484	1.46
	WBz	5500	5950(?)	0.502	1.44
		Azo acid dyes			
II	BzOH	4200(?)	5230	0.820	0.30(?)
	W	4150(?)	5030	0.740	0.328(?)
				1.970	0.331(?)
	WBz	4200(?)	5150	0.760	0.30(?)
		4240(?)	5100	1.890	0.29(?)
	WD	4200(?)	5150	0.760	0.34(?)
	WI	4150(?)	5050	0.740	0.33(?)

cont'd.

Table V cont'd

IV	W	4250(?)	5050	0.740	0.28(?)
				1.85	0.29(?)
	WBz	4250(?)	5100	0.740	0.24(?)
				1.750	0.26(?)

*BzOH = pure benzyl alcohol; W = water; WBz = 3% (vol/vol) benzyl alcohol-water; WD = 50:50 (vol/vol) water-dioxan; WG = 3% (wt/vol) aqueous glucose solution; WI = 3% (wt/vol) aqueous meso-inositol solution.

Table VI

External Surface Area Data for Different Fibres

Solvent	Solute	External Surface Area ($cm^2/gm.$)			
		Nylon	Wool A	Terylene	Cuprammonium Rayon
n-Heptane	Phenol	360			
Toluene	PNP	405			
Xylene	PNP	495			
Cyclo-Hexane-Xylene(70:30)	PNP	990			
n-Hexane	PNP	1305	1530	1188	2430
n-Heptane	PNP	1300		1260	
Cyclo-Hexane	PNP	1692			
Iso-Octane	PNP	2420	945		
Cyclo-Hexane (Diox.*)	PNP	2970	765		
n-Hexane (Diox.*)	PNP		900		
n-Hexane (n-Bu.*)	PNP		1035		
Water	Rhodamine B		7590		
Water	Rhodamine 6 GB		51600		
Microscopic method		1593	1271	1389	2372
Air-permeability method		1447	1592	1788	2748

Diox. = Dioxan; n-Bu. = n-Butanol.

*Solvent in parentheses denotes the solvent used for initial dissolution of solute (usually a drop).

Table VII

External Surface Area Data for Different Wool Fibres

Solvent	Solute	External Surface Area ($cm^2/gm.$)			
		Wool A	Wool B	Wool C	Wool D
Hexane	PNP	1530	3240	2070	1710
Iso-Octane	PNP	945	4310		1440
Microscopic method		1271	1272	1238	1136
Air-permeability method		1592	1593	1590	1531

Table VIII

Surface Area Data for Paper Samples

Sample	S.A. ($cm^2/gm.$) ads. method.	Drainage Rate - S.R.° *	Fibre Length Index*	Freeness value‡	S.A. ($cm^2/gm.$) ⁄
1	7020	9	4.45	890	7,700
2	8822	14	2.75	740	10,450
3	9225	20	1.59	600	12,250

*Supplied by T. B. Ford Ltd., High Wycombe.

‡Value obtained from Ref. 130 for corresponding Drainage Rate values.

⁄S.A. calculated from results on wood pulp from 131 corresponding to Drainage Rate values.

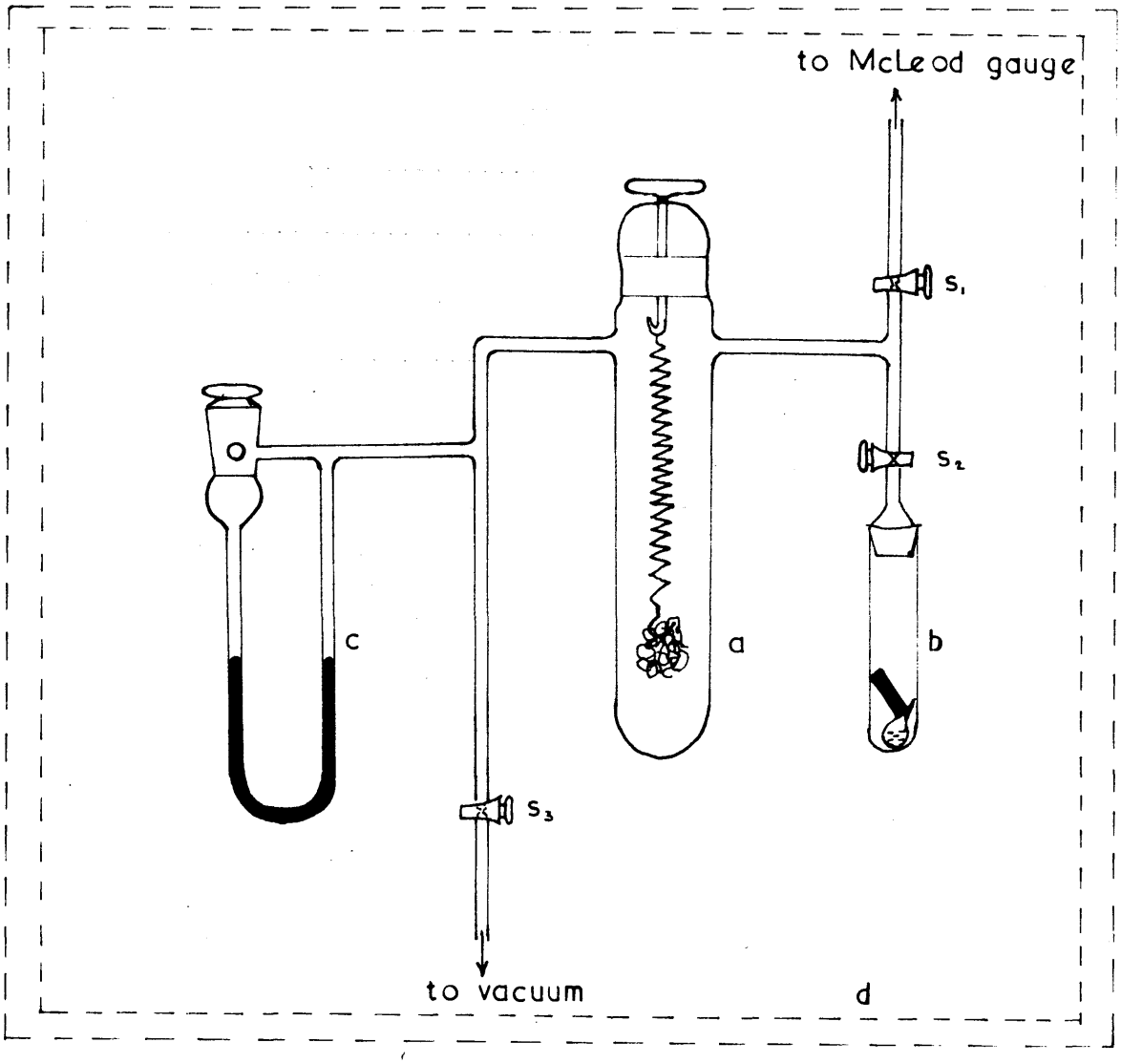


FIG.1. Vapour phase adsorption apparatus:

a: Adsorption chamber.
b: Liquid tube.
c: Manometer.
d: Air thermostat.
s_1, s_2, s_3: Stop-cocks.

LEGENDS TO FIG.2.

Rate curves for methyl alcohol on Lincoln fleece wool.

○ Clean wool.

● Wool dyed with Irgalan Brown 2 GL.

◑ Wool dyed with Solway Blue BN.

◐ Wool containing silver chromate.

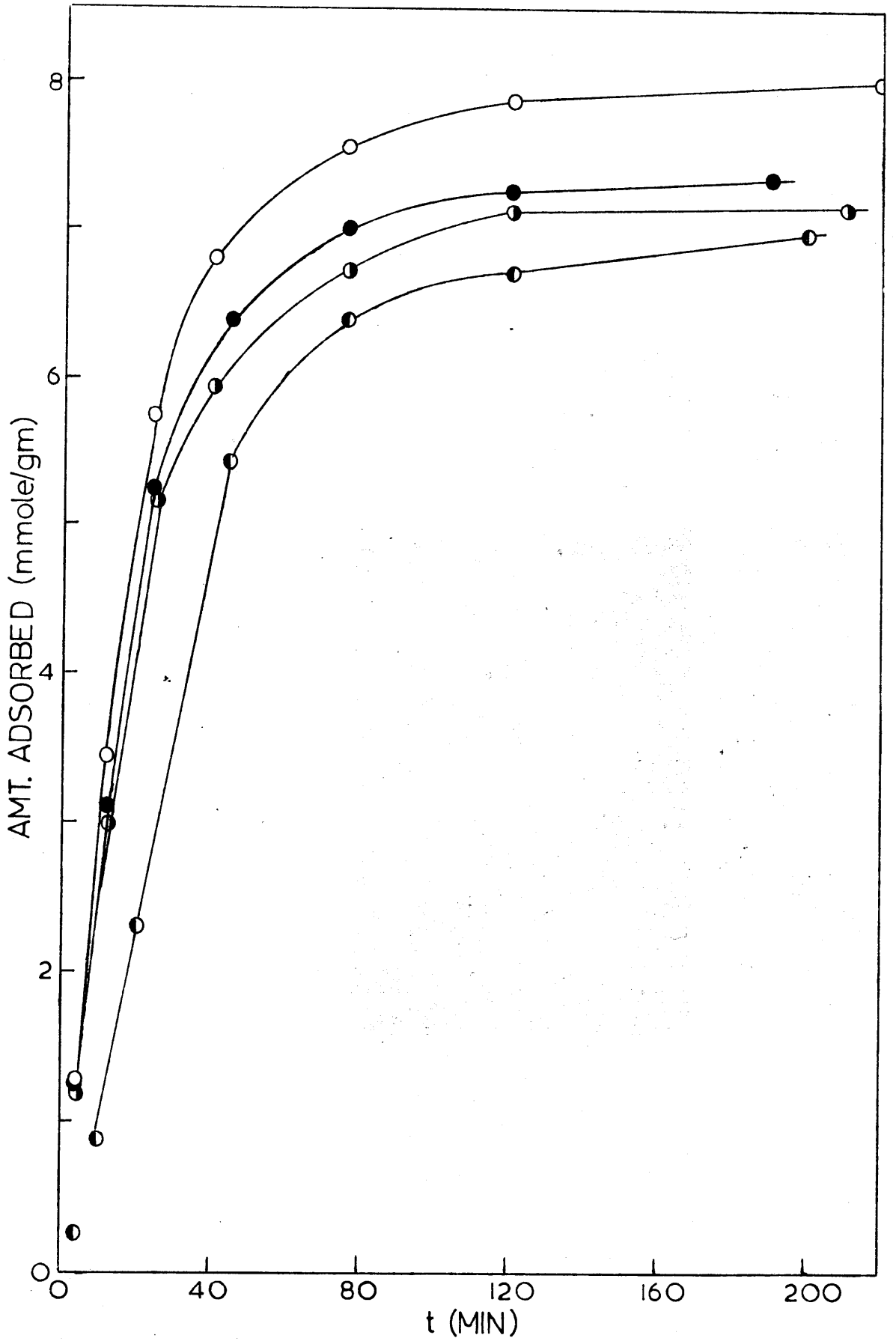


FIG.2.

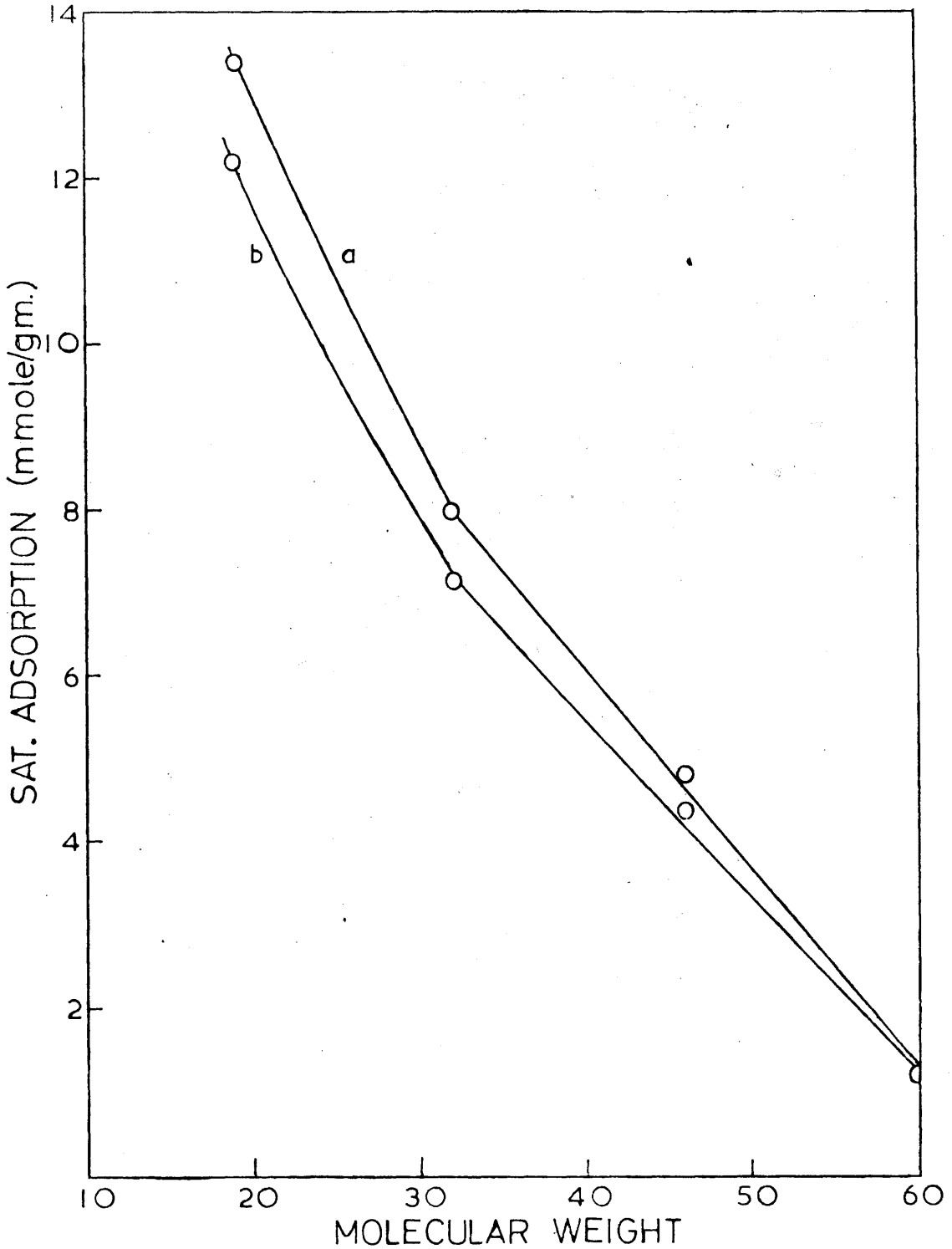


FIG.3. Relation between saturation adsorption and molecular weight of different vapours used in present work (Lincoln fleece wool).

a: clean wool.

b: Solway Blue BN dyed wool.

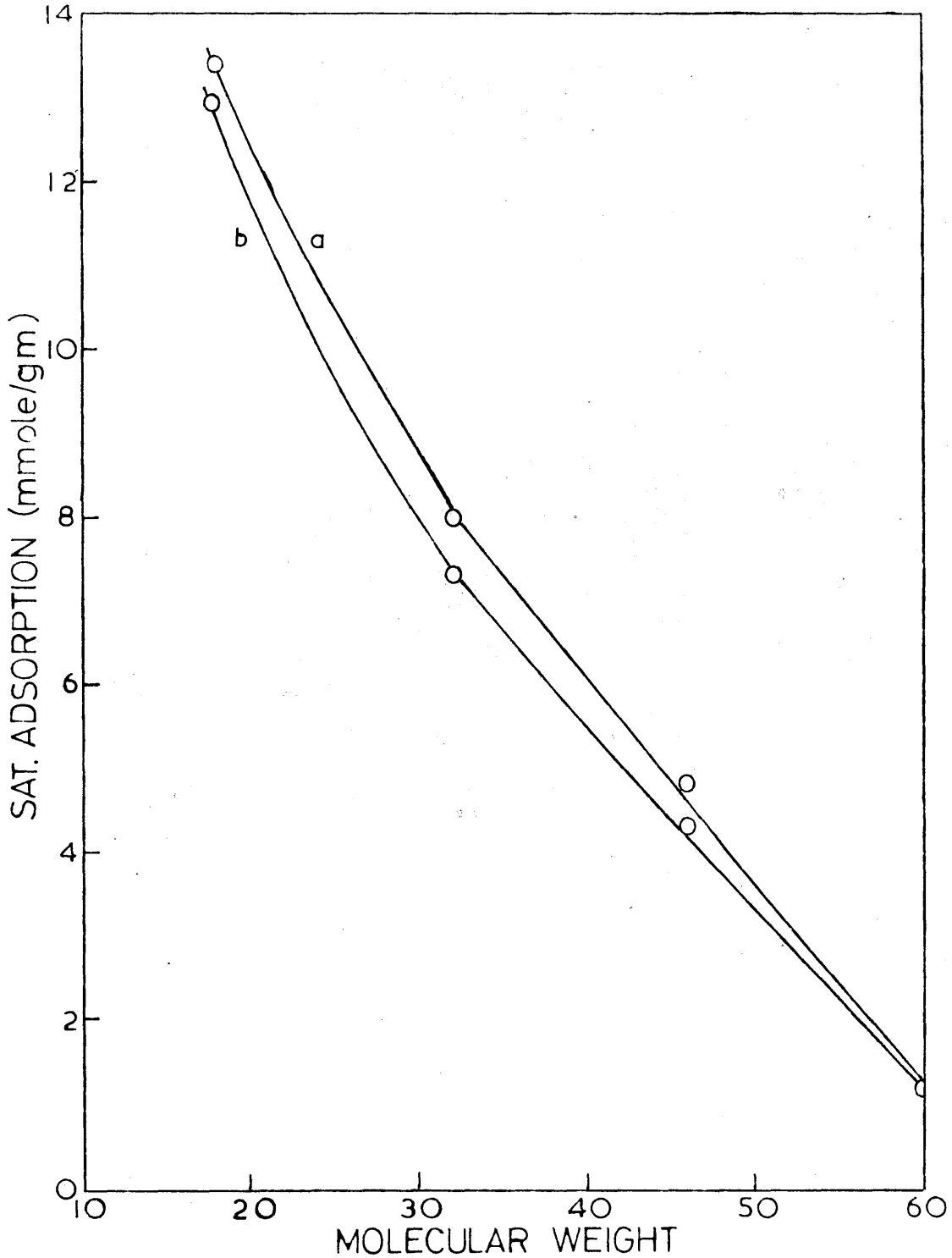


FIG.4. Relation between saturation adsorption and molecular weight of different vapours used in present work (Lincoln fleece wool).

a: Clean wool.

b: Irgalan Brown 2 GL dyed wool.

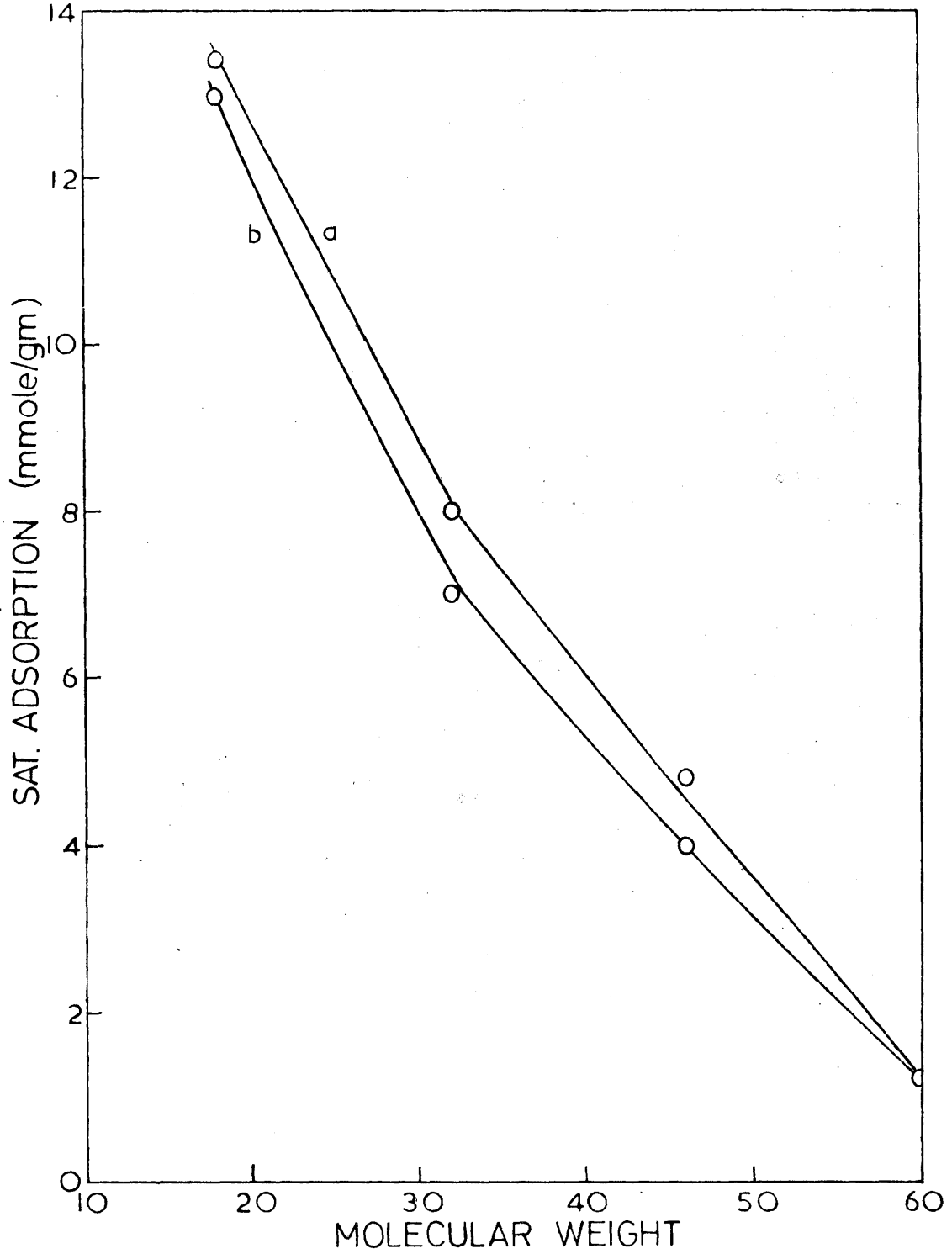


FIG.5. Relation between saturation adsorption and molecular weight of different vapours used in present work (Lincoln fleece wool).

a: Clean wool.

b: Silver chromate - containing wool.

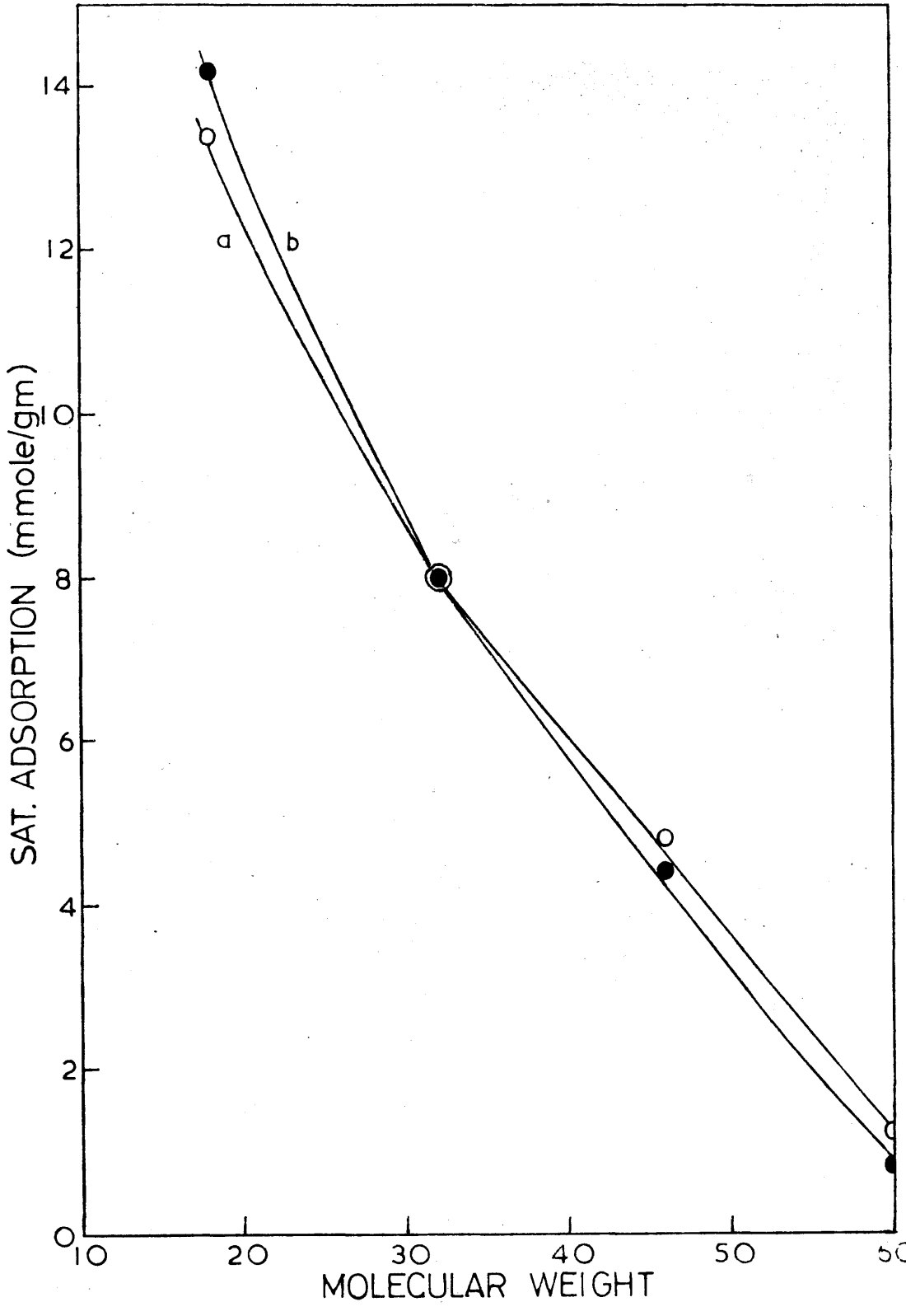


FIG.6. Comparison of adsorption properties of Lincoln fleece wool and Australian merino wool for different vapours used in present work.

a: Lincoln fleece wool.

b: Australian merino wool.

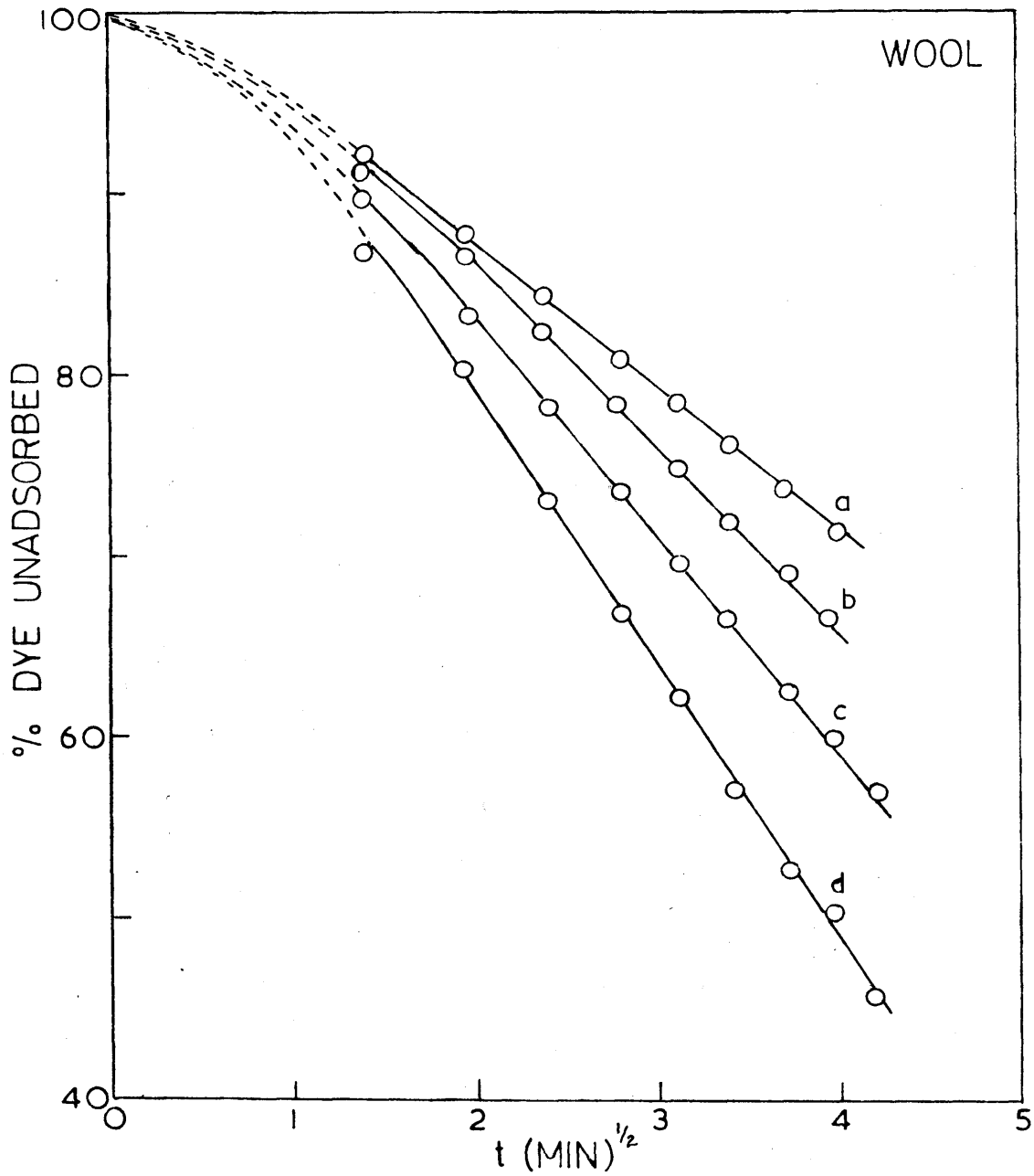


FIG.7. Typical rate curves for dyes on wool:

a: dye I ; b: dye IV ; c: dye III ; d: dye II.

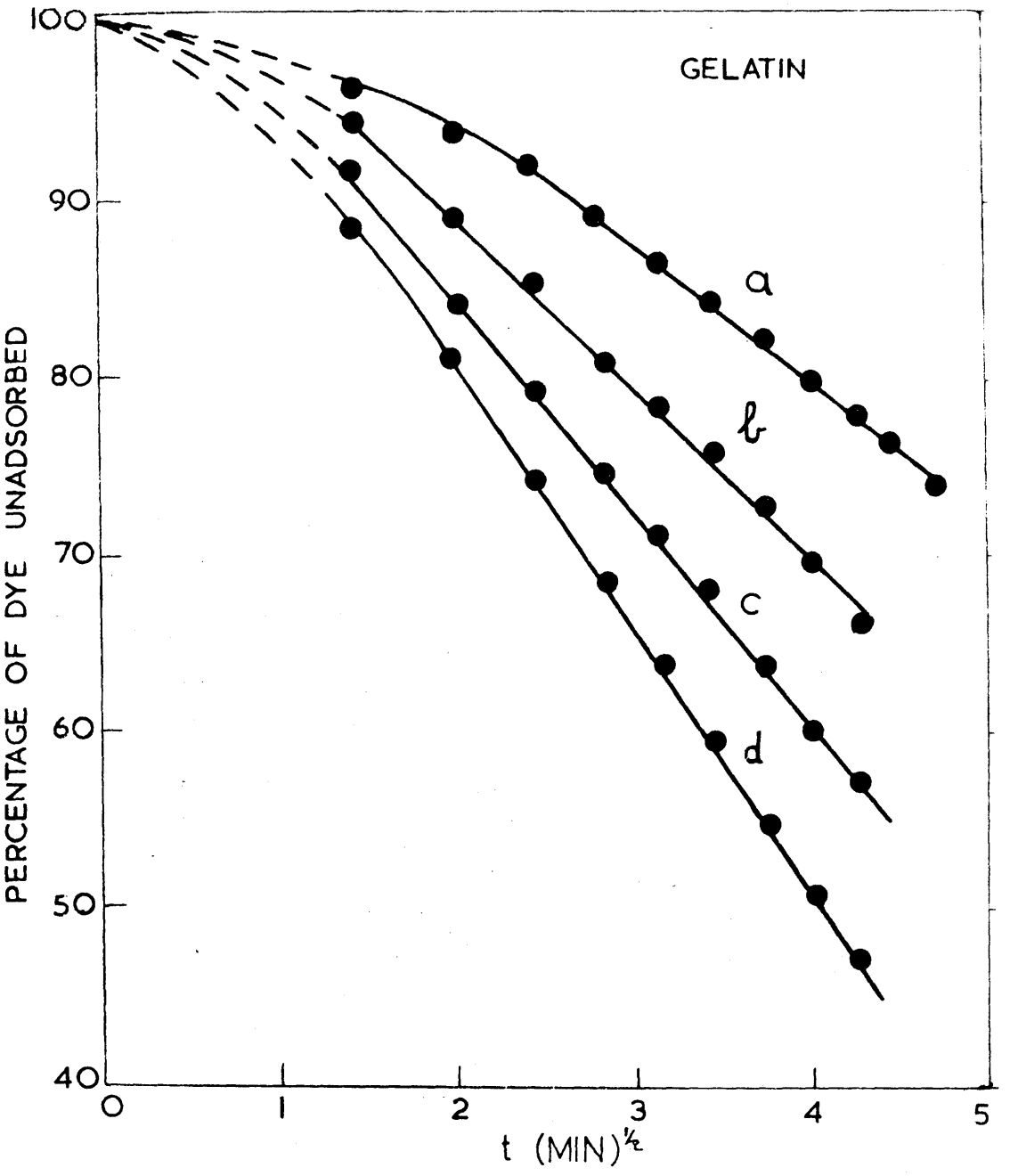


FIG.8. Typical rate curves for dyes on gelatin:

a: dye I ; b: dye IV ; c: dye III ; d: dye II.

LEGENDS TO FIG.9.

Relation between number of added substituent groups in dye molecules and (log) relative dyeing rate in wool.

a: dyes II, III, IV, no solvent.

a': dyes II, III, IV, from 3% (vol./vol.) benzyl alcohol.

d: dyes Va, Vb, Vc, Vd.

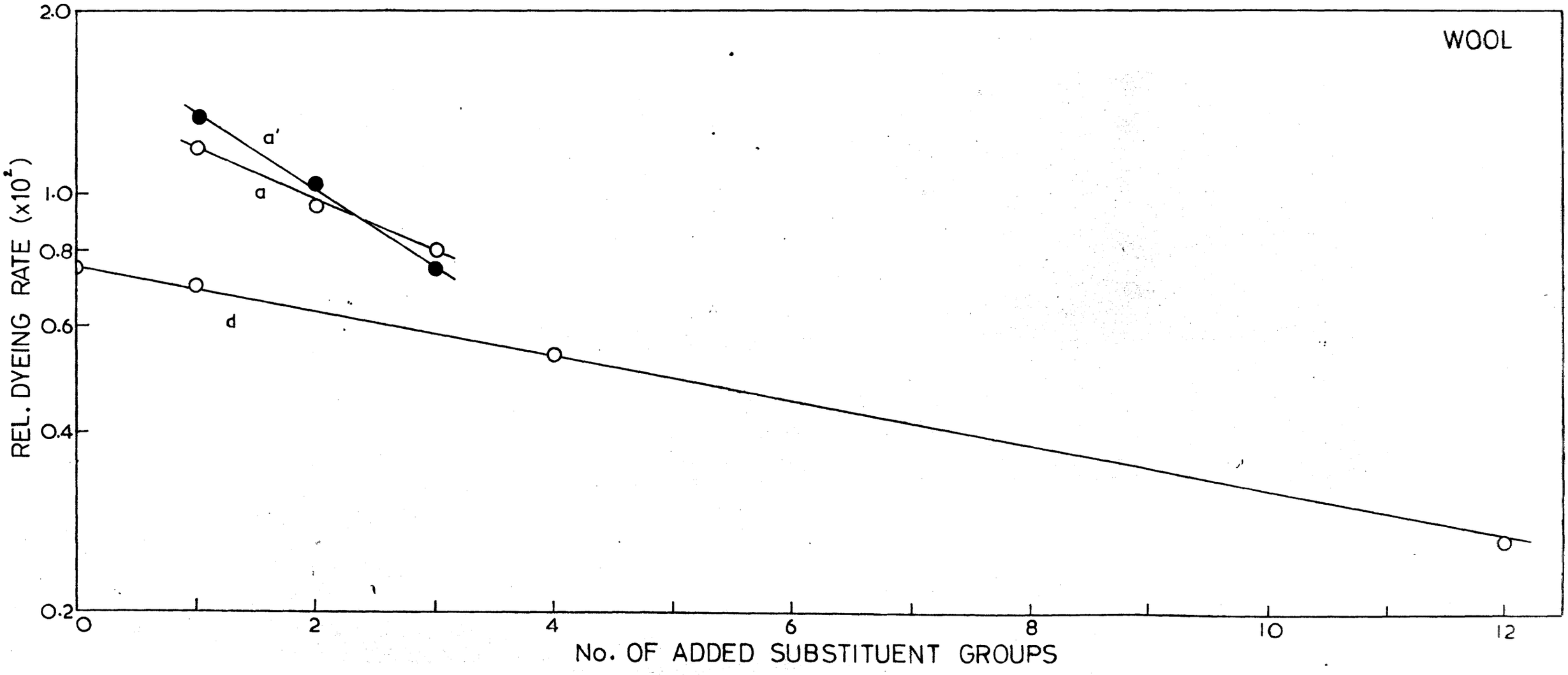

WOOL
REL. DYEING RATE (x10²)
2.0
1.0
0.8
0.6
0.4
0.2
a'
a
d
0
2
4
6
8
10
12
No. OF ADDED SUBSTITUENT GROUPS

FIG.9.

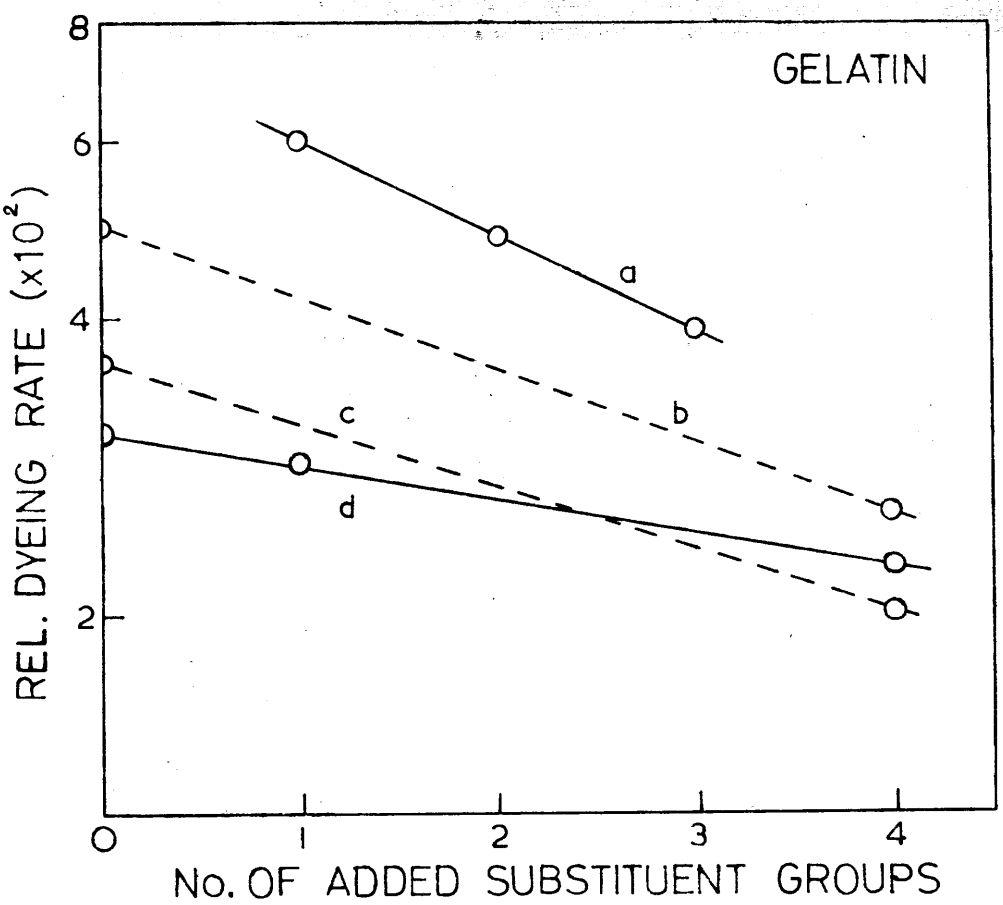


FIG.10. Relation between number of added substituent groups in dye molecules and (log) relative dyeing rate in gelatin.

a: dyes II, III, IV.

b: dyes VIa, VIb.

c: dyes X, XI.

d: dyes Va, Vb, Vc.

LEGENDS TO FIG.11.

Relation between molecular volume of acid dyes and (log) relative dyeing rate in wool.

a: dyes II, III, IV.

d: dyes Va, Vb, I, Vc, Vd.

e: dye VII.

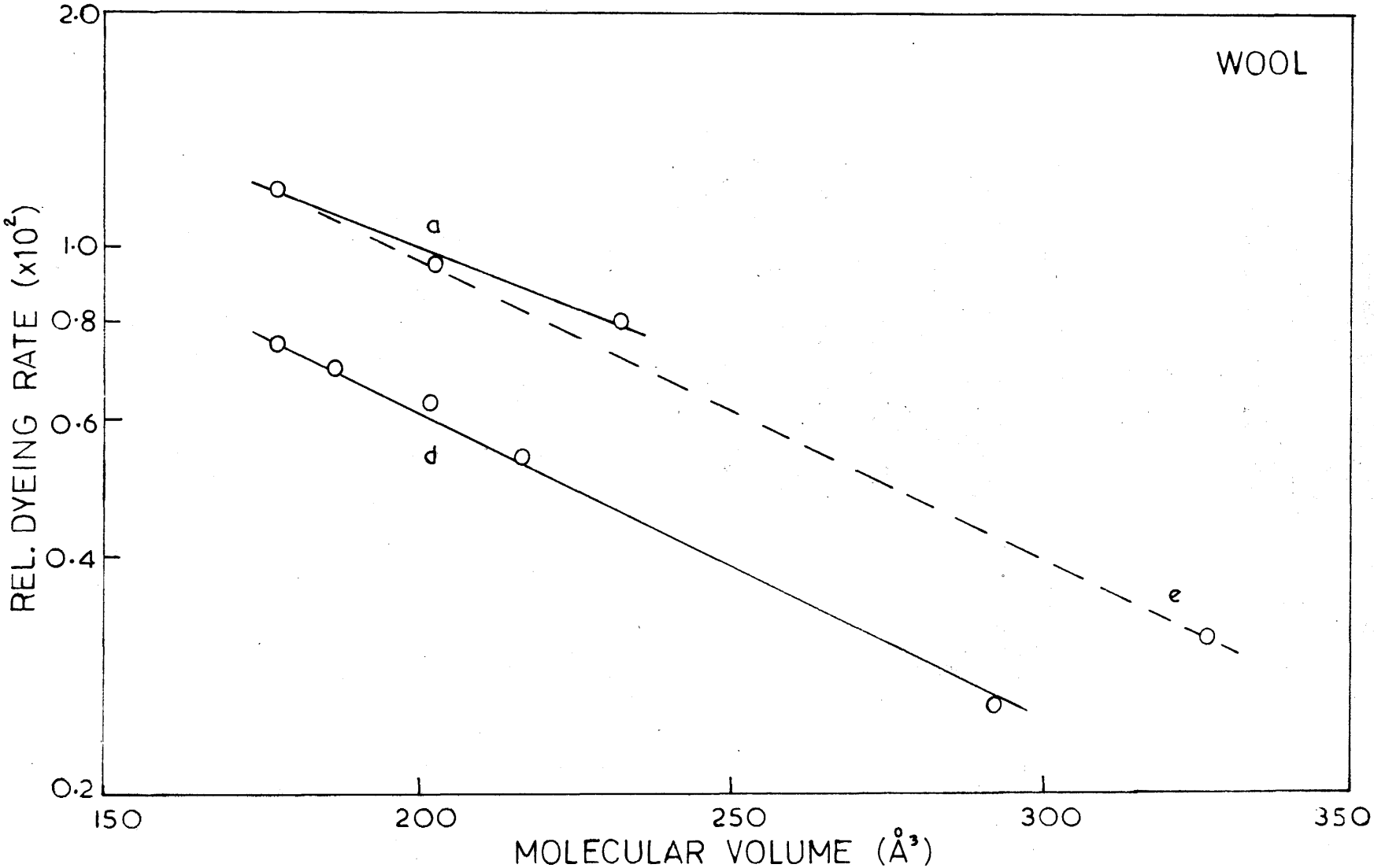

WOOL
REL. DYEING RATE (x10²)
2·0
1·0
0·8
0·6
0·4
0·2
150
200
250
300
350
MOLECULAR VOLUME (Å³)
a
d
e

FIG.11.

LEGENDS TO FIG.12.

Relation between molecular volume of acid dyes and (log) relative dyeing rate in gelatin.

a: dyes II, III, IV.

b: dyes VIa, VIb.

c: dyes X, XI.

d: dyes Va, Vb, I, Vc.

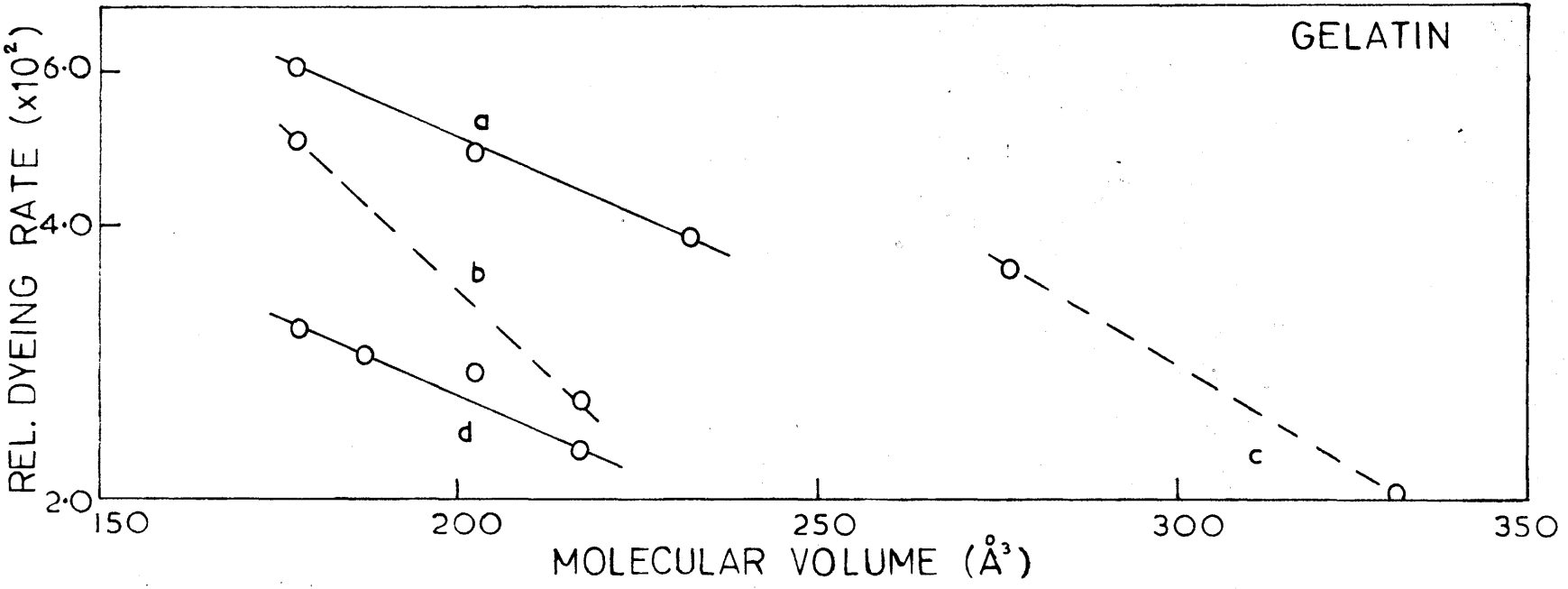

GELATIN
REL. DYEING RATE (x10²)
6·0
4·0
2·0
150
200
250
300
350
MOLECULAR VOLUME (Å³)
a
b
c
d

FIG.12.

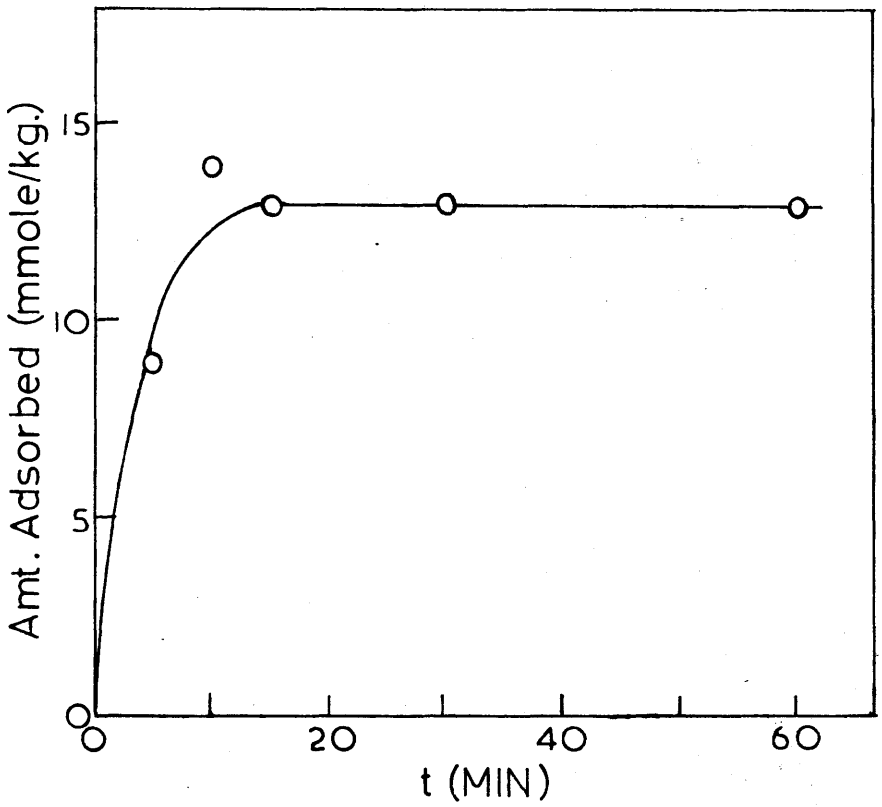


FIG.13. Rate of adsorption of benzyl alcohol on wool from a 50 mmole/litre solution at 21°C.

LEGENDS TO FIG.14.

Relation between c_t/c_∞ and $t^{1/2}$, for dyes II and IV on wool, used for obtaining values of apparent diffusion coefficient. Average fibre radius, 12.08μ.

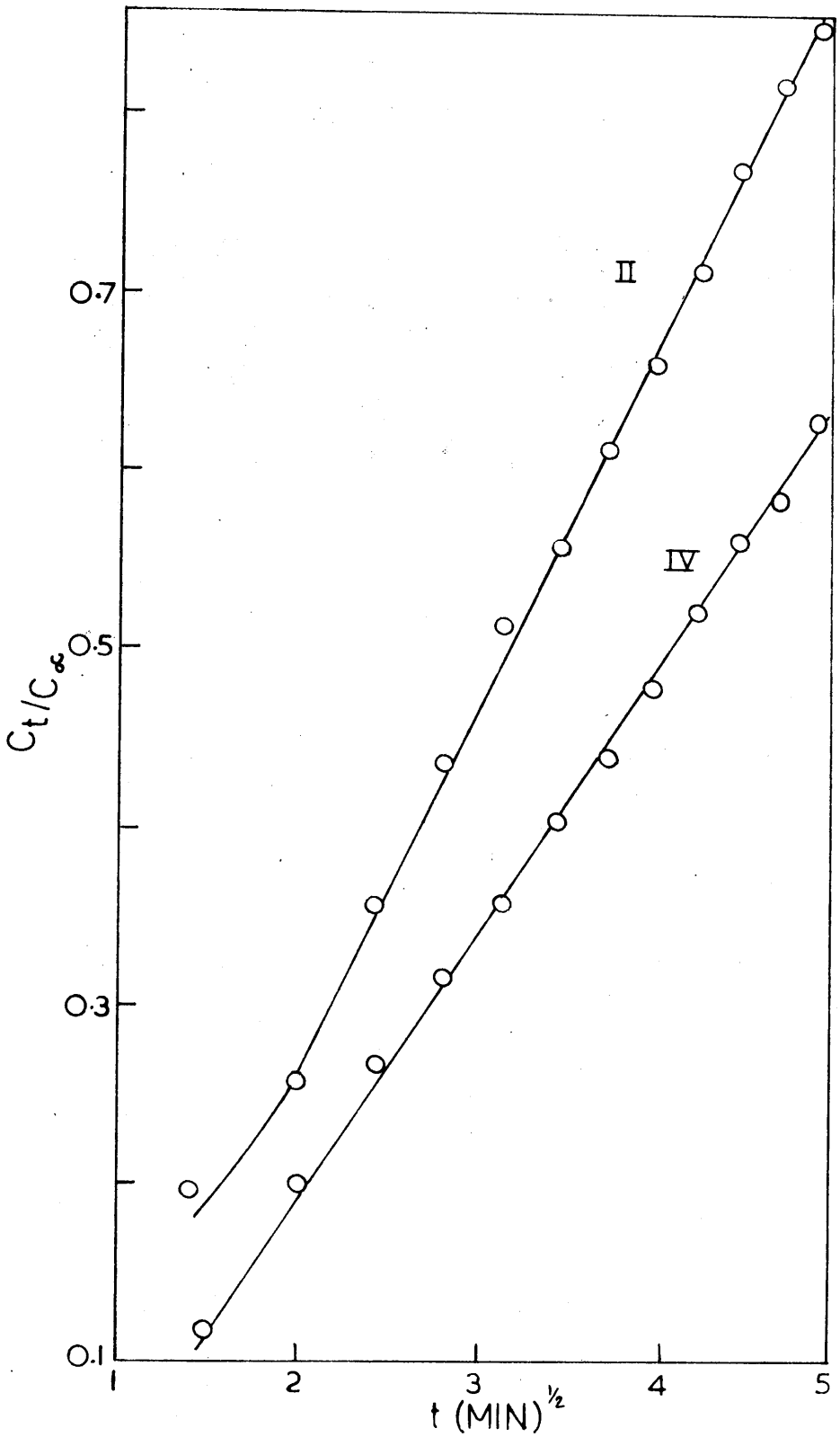


FIG.14.

LEGENDS TO FIG.15.

Relation between number of carbon atoms in acid dye molecules and their respective wash fastness number. (Colour Index data).

– indicate additional points.

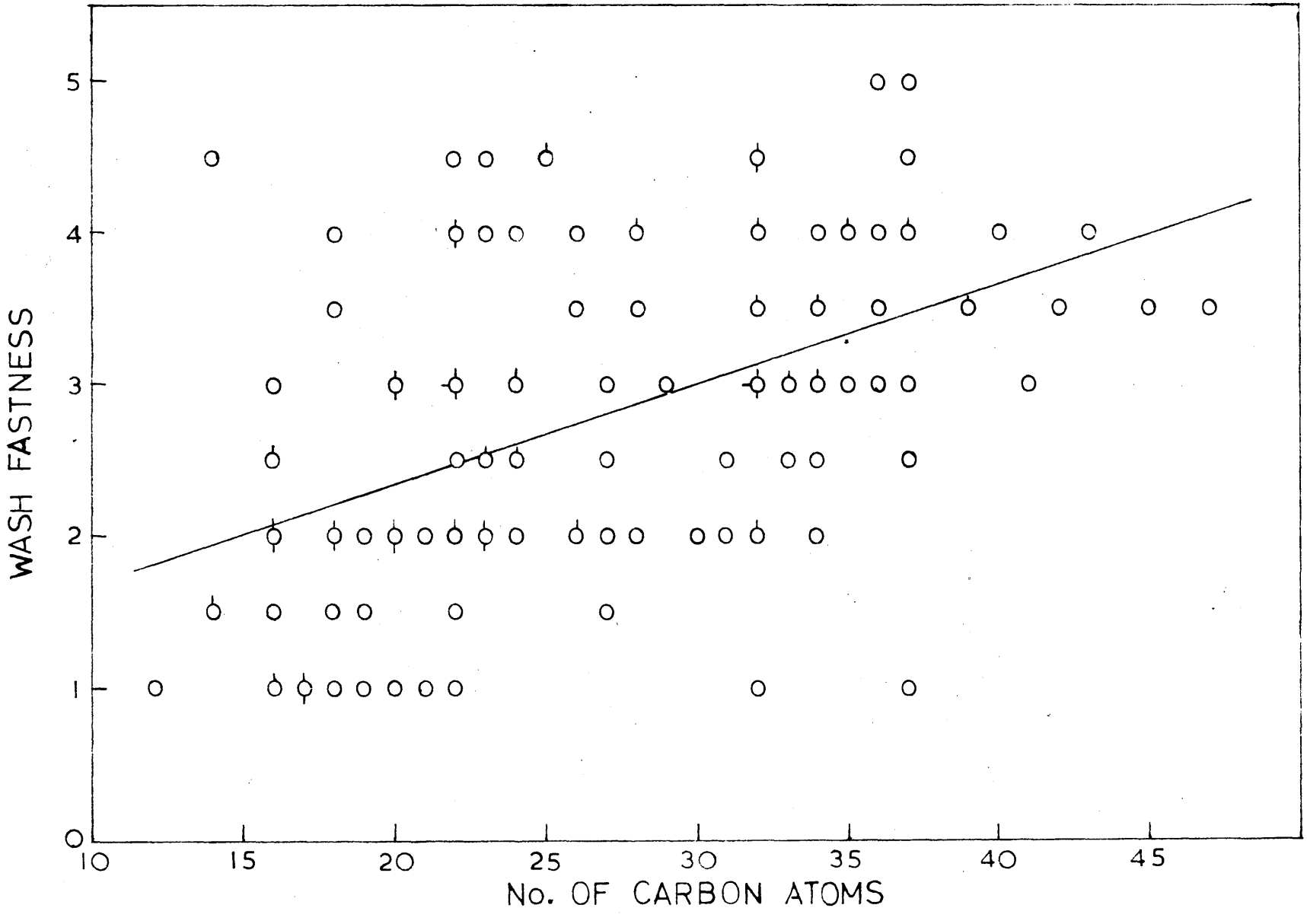


FIG.15.

LEGENDS TO FIG.16.

Relation between number of carbon atoms in acid dye molecules and their respective migration number. (Colour Index data).

– indicate additional points.

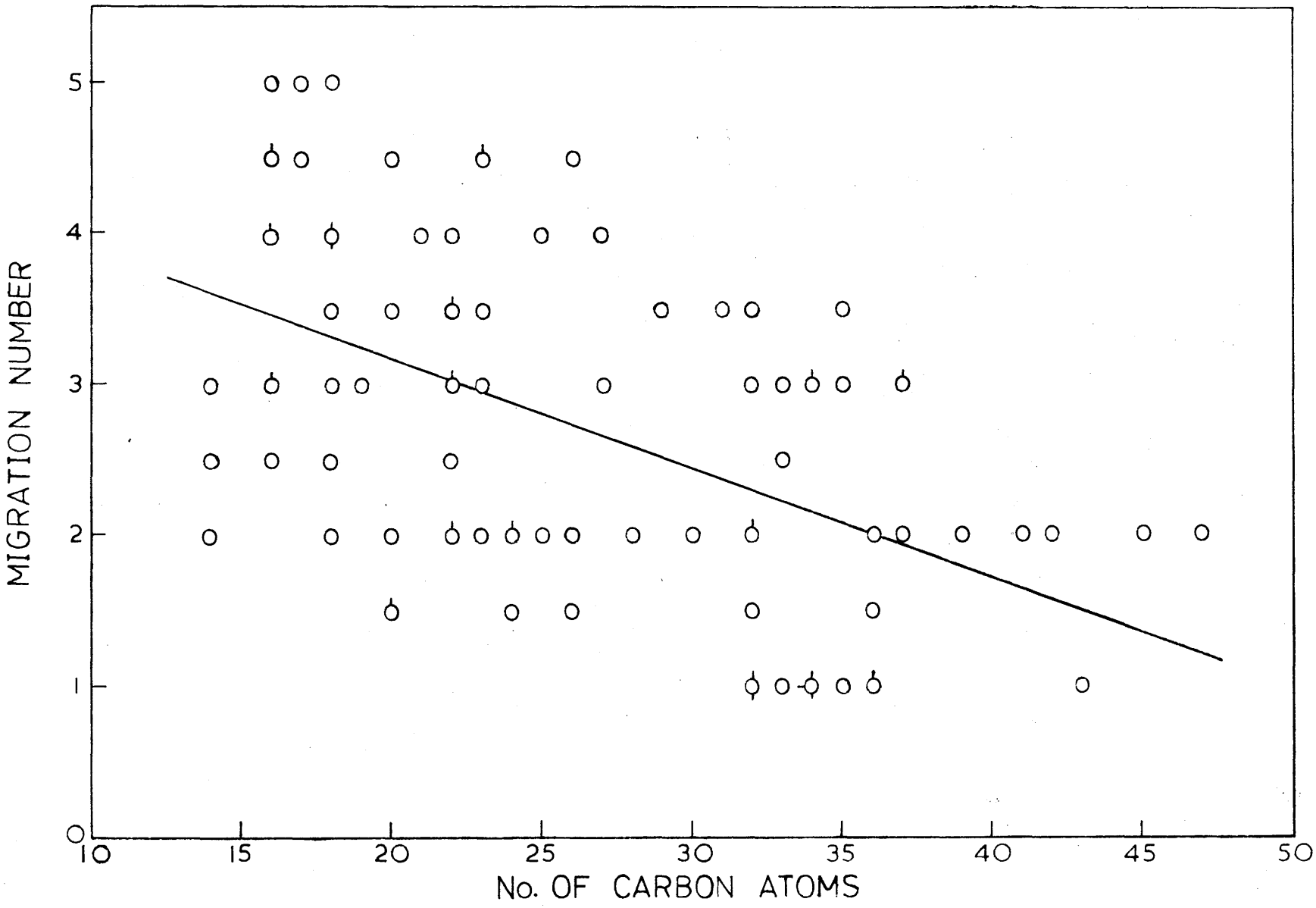

MIGRATION NUMBER
0
1
2
3
4
5
10
15
20
25
30
35
40
45
50
No. OF CARBON ATOMS

FIG. 16.

LEGENDS TO FIG.17.

Relation between the total number of atoms in acid dye molecules and their respective wash fastness number. (Colour Index data).
- indicate additional points.

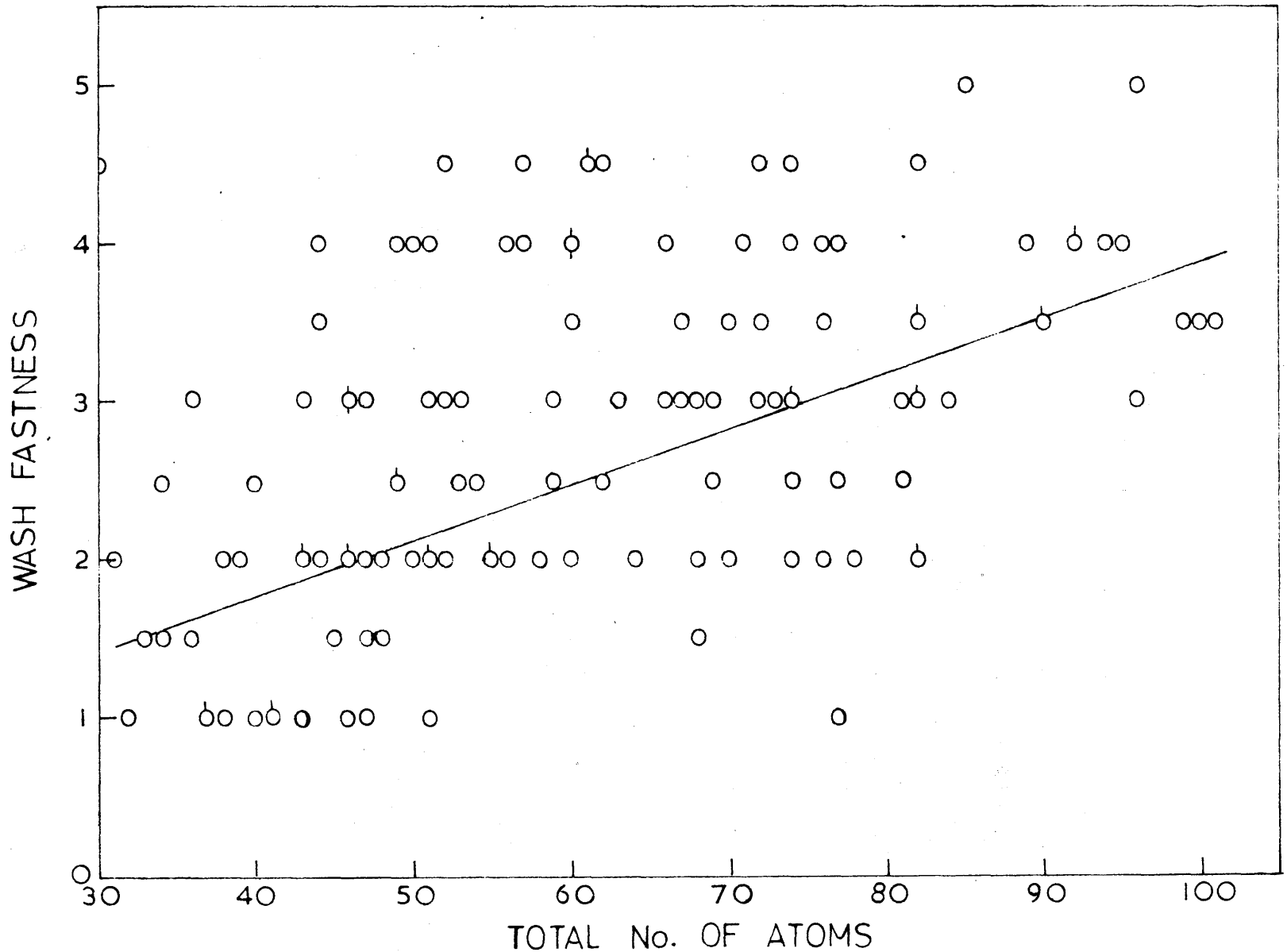


FIG. 17

LEGENDS TO FIG.18.

Relation between the total number of atoms in acid dye molecules and their respective migration number. (Colour Index data).

- indicate additional points.

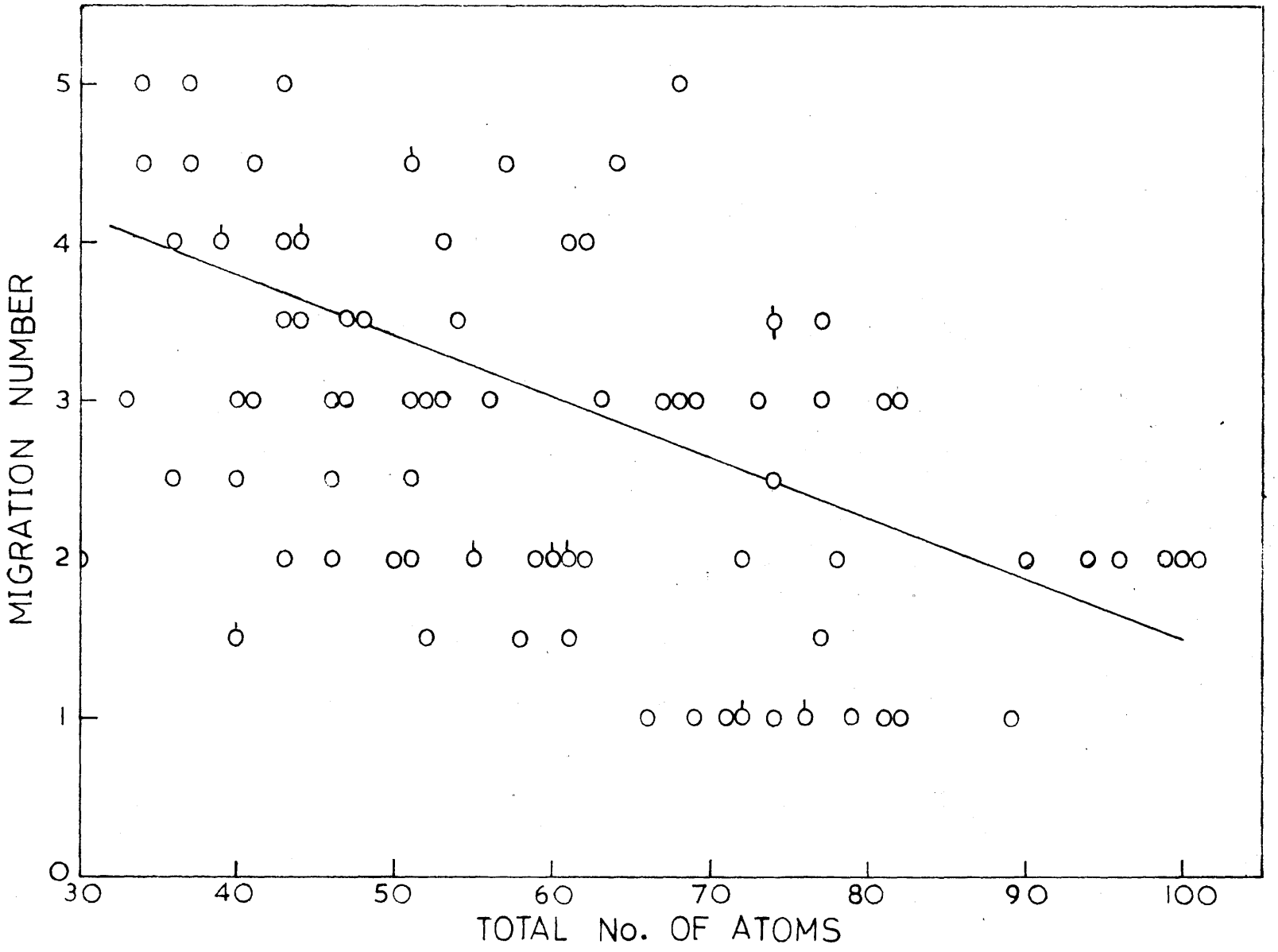

MIGRATION NUMBER
0
1
2
3
4
5
30
40
50
60
70
80
90
100
TOTAL No. OF ATOMS

FIG.18

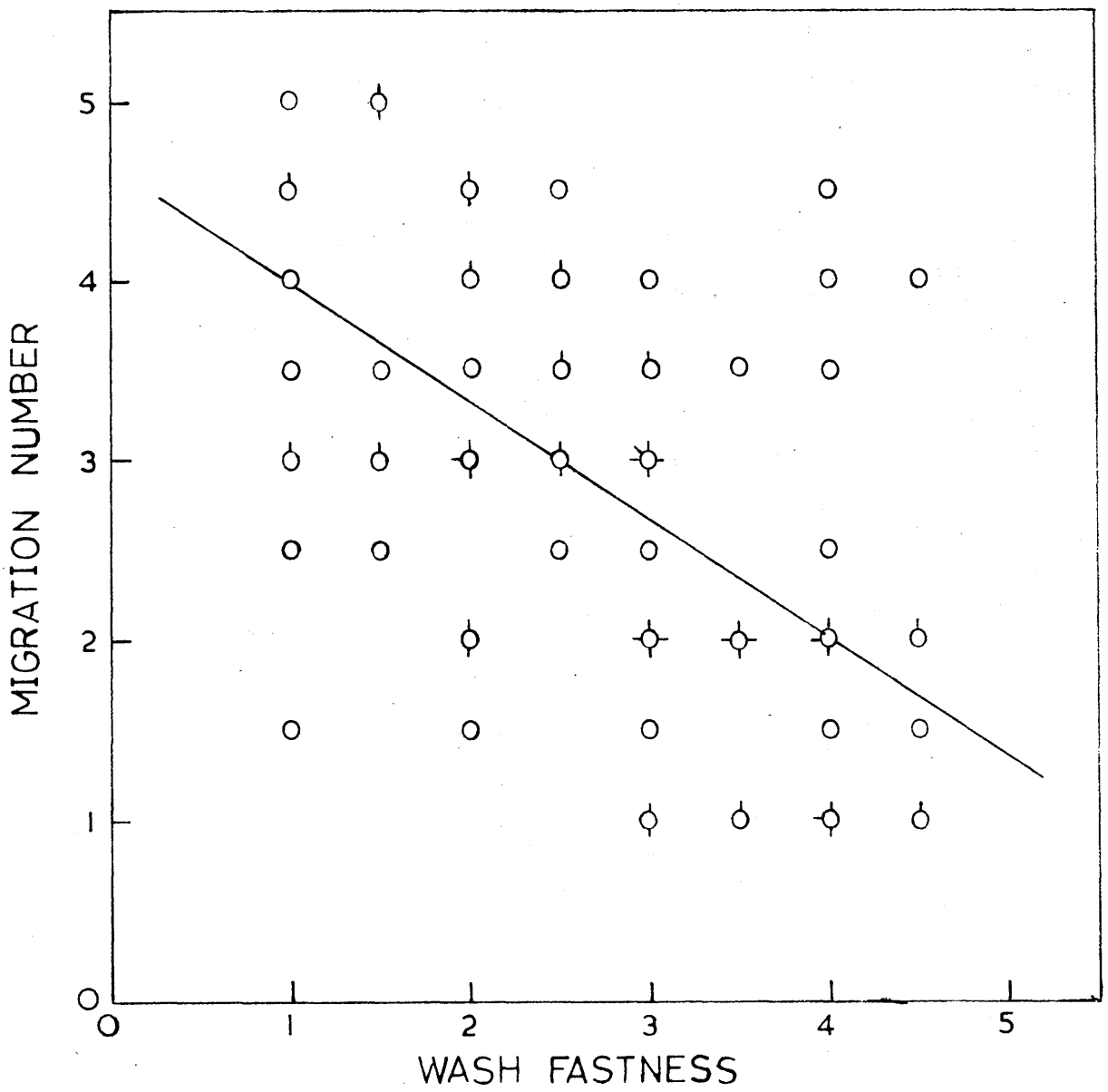


FIG.19. Relation between the wash fastness number and migration number of acid dyes (Colour Index data). - indicate additional points.

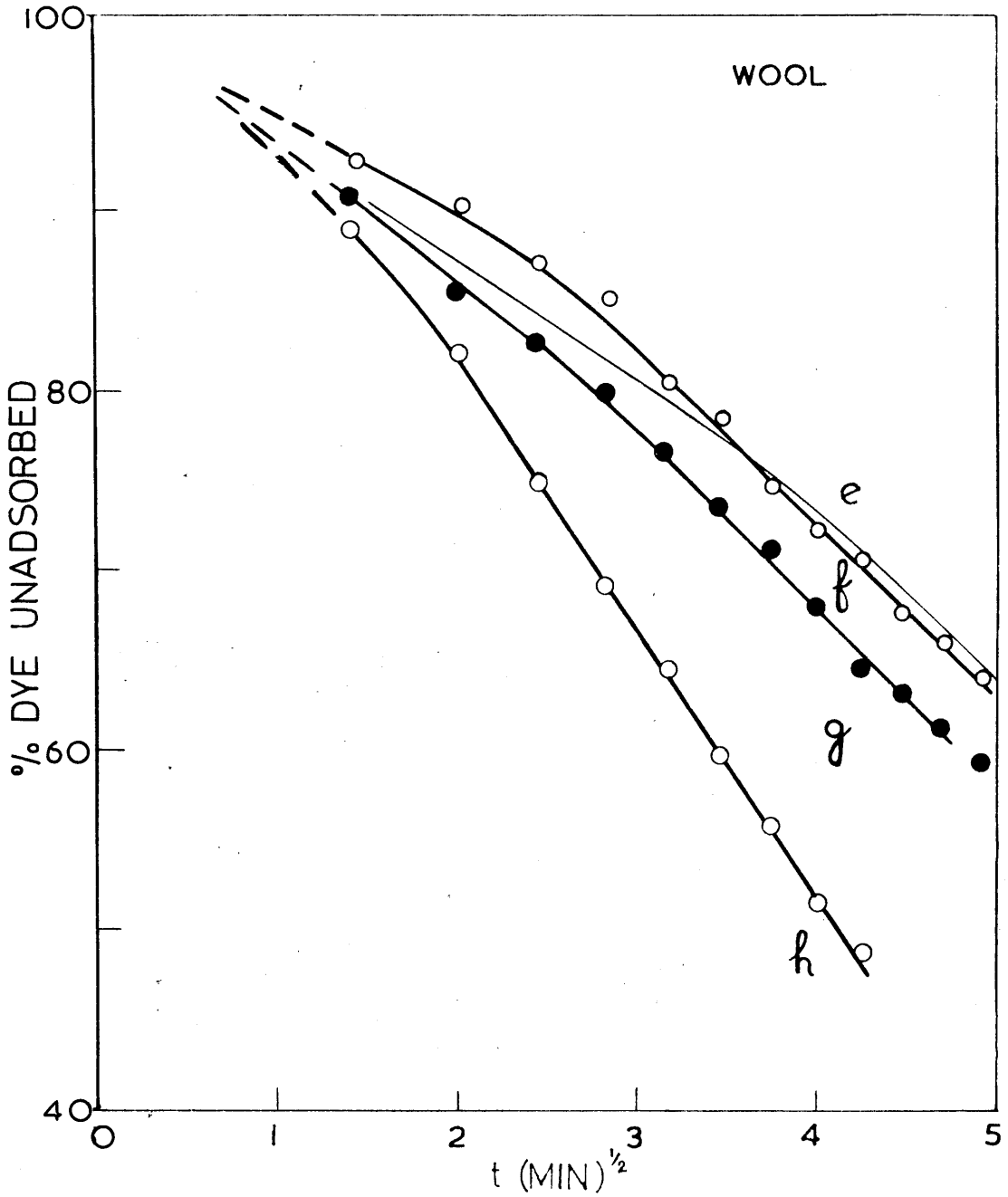


FIG.20. Rate curves for dye VIII on wool.

e: D-glucose, meso-inositol (both at 3% wt/vol, give the same curve. Experimental points omitted for clarity).
f: No solvent.
g: 3% (vol/vol) dioxan.
h: 3% (vol/vol) benzyl alcohol.

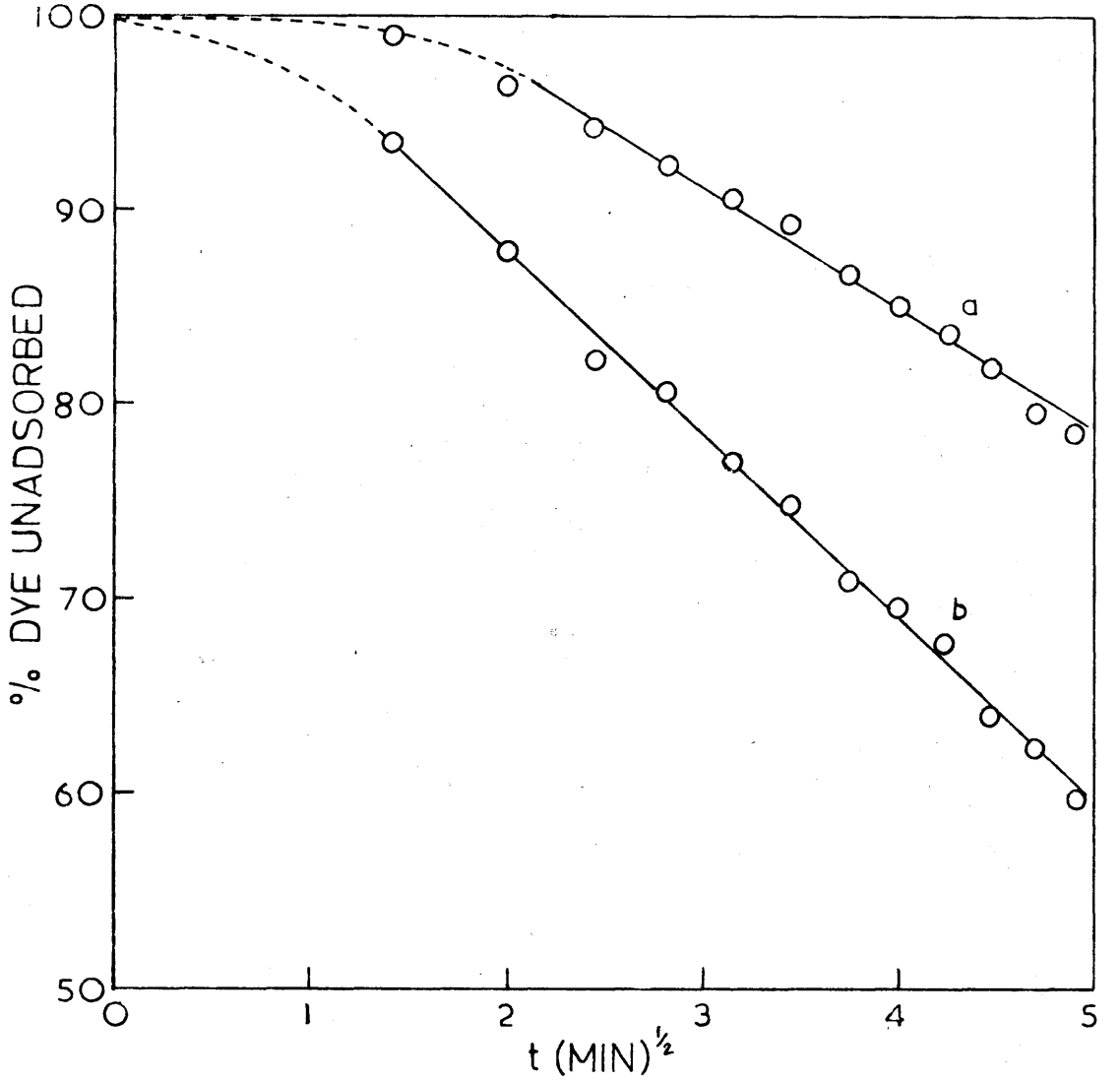


FIG.21. Rate curves for dye VIII on gelatin.

a: No solvent.

b: 3% (vol/vol) benzyl alcohol.

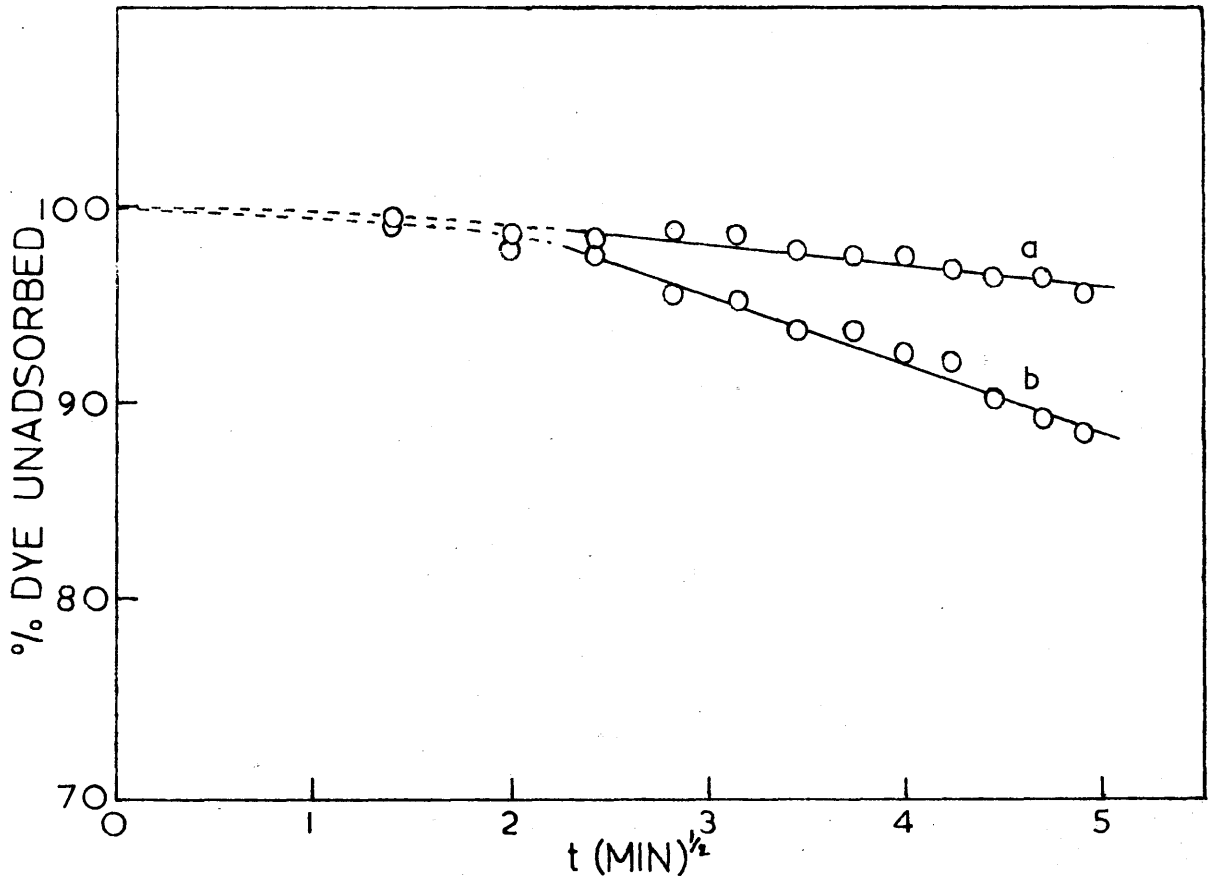


FIG.22. Rate curves for dye VIII on nylon.

a: no solvent.

b: 3% (vol/vol) benzyl alcohol.

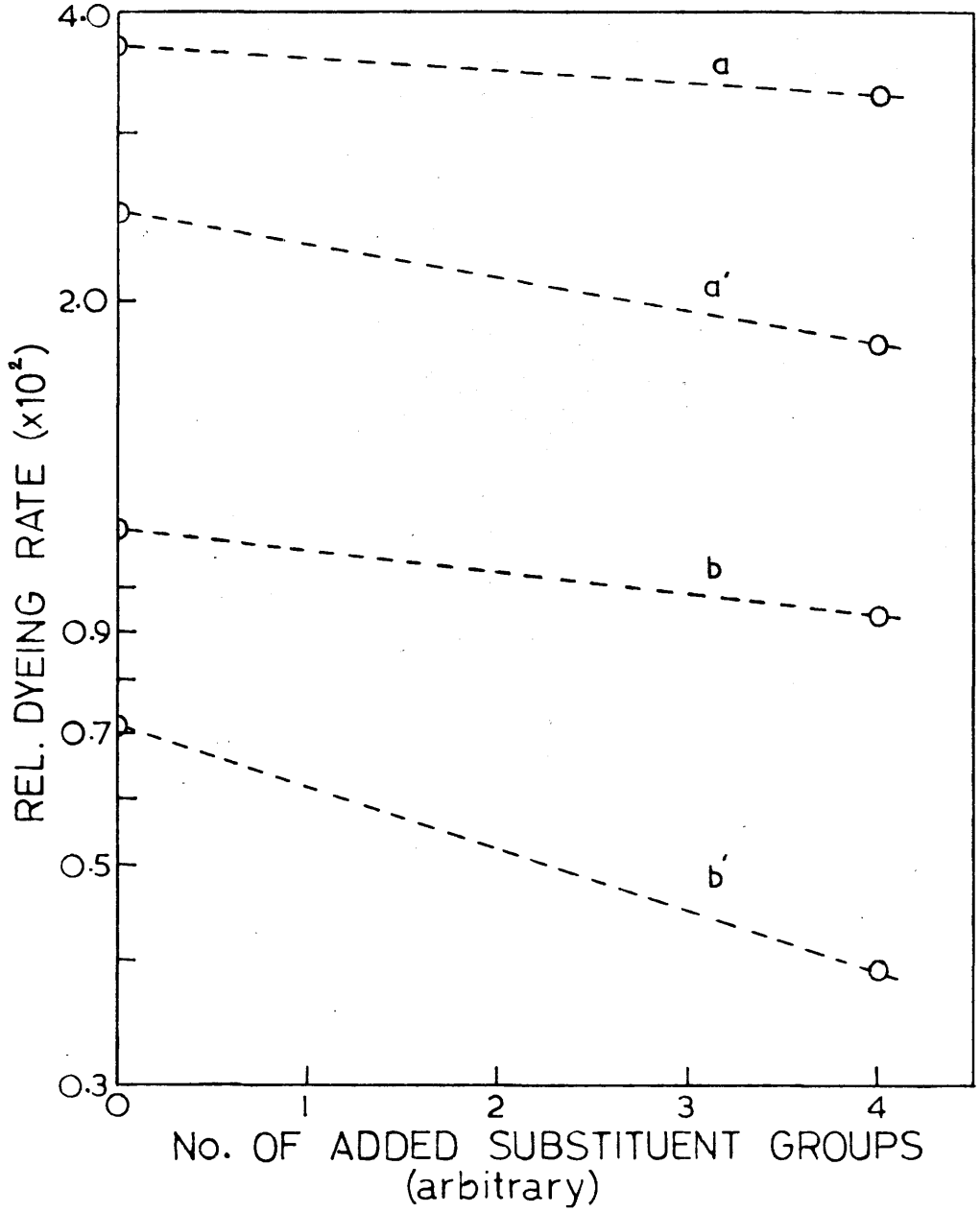


FIG.23. Relation between the arbitrary number of added substituent groups for dyes VIII and IX (structural formulae of these dyes being unknown) and (log) relative dyeing rate in gelatin and wool, to show the magnitude of effect on dyeing rate in presence of 3% (vol/vol) benzyl alcohol.

Gelatin: a: 3% (vol/vol) benzyl alcohol.
a': no solvent.
Wool: b: 3% (vol/vol) benzyl alcohol.
b': no solvent.

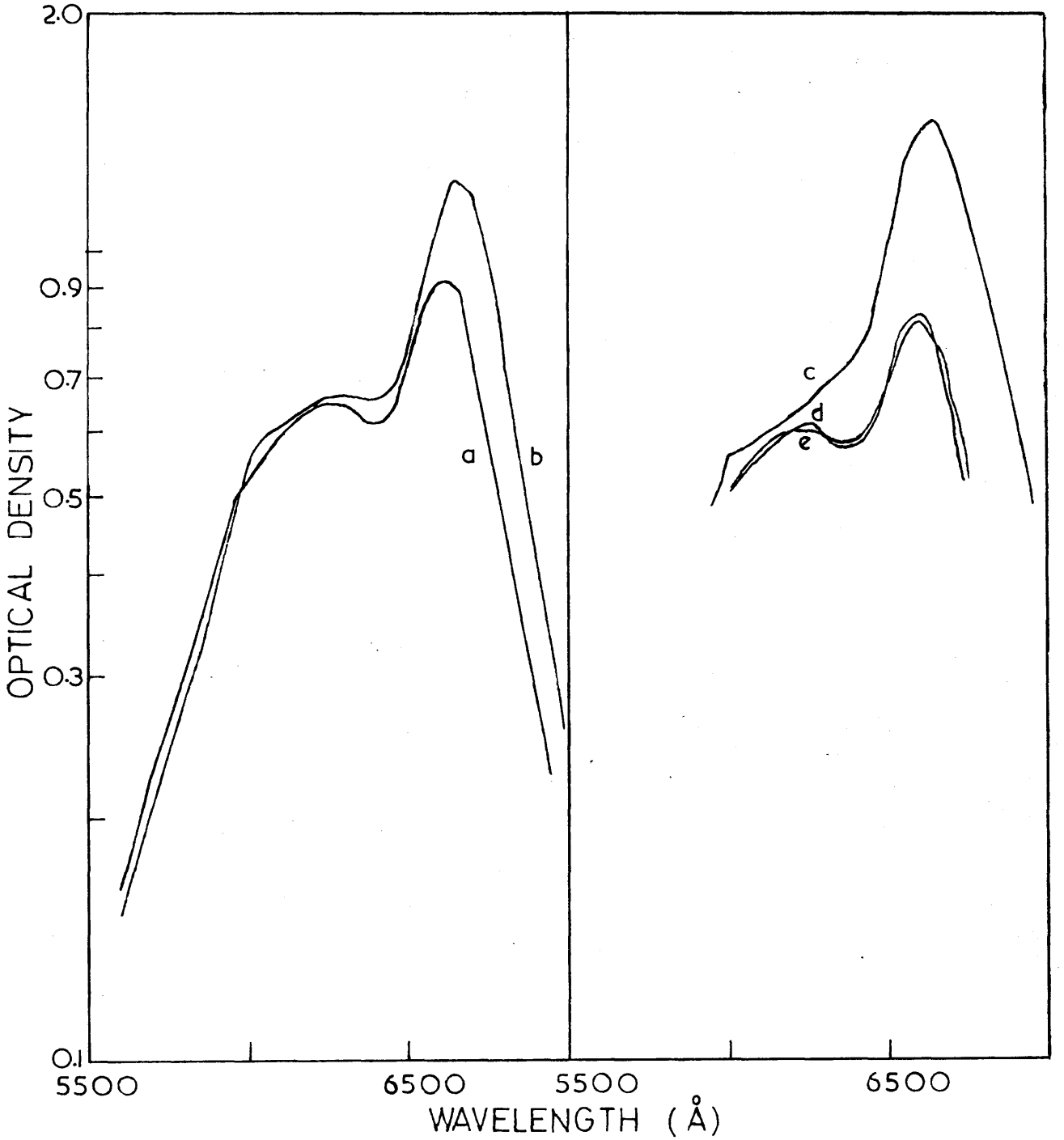


FIG.24. Spectral curves for Procion Brill. Blue H7G (I.C.I.)

a: no solvent ; b: 3% (vol/vol) benzyl alcohol ;
c: 50% (vol/vol) dioxan ; d: 3% (wt/vol) meso-inositol ;
e: 3% (wt/vol) D-glucose.

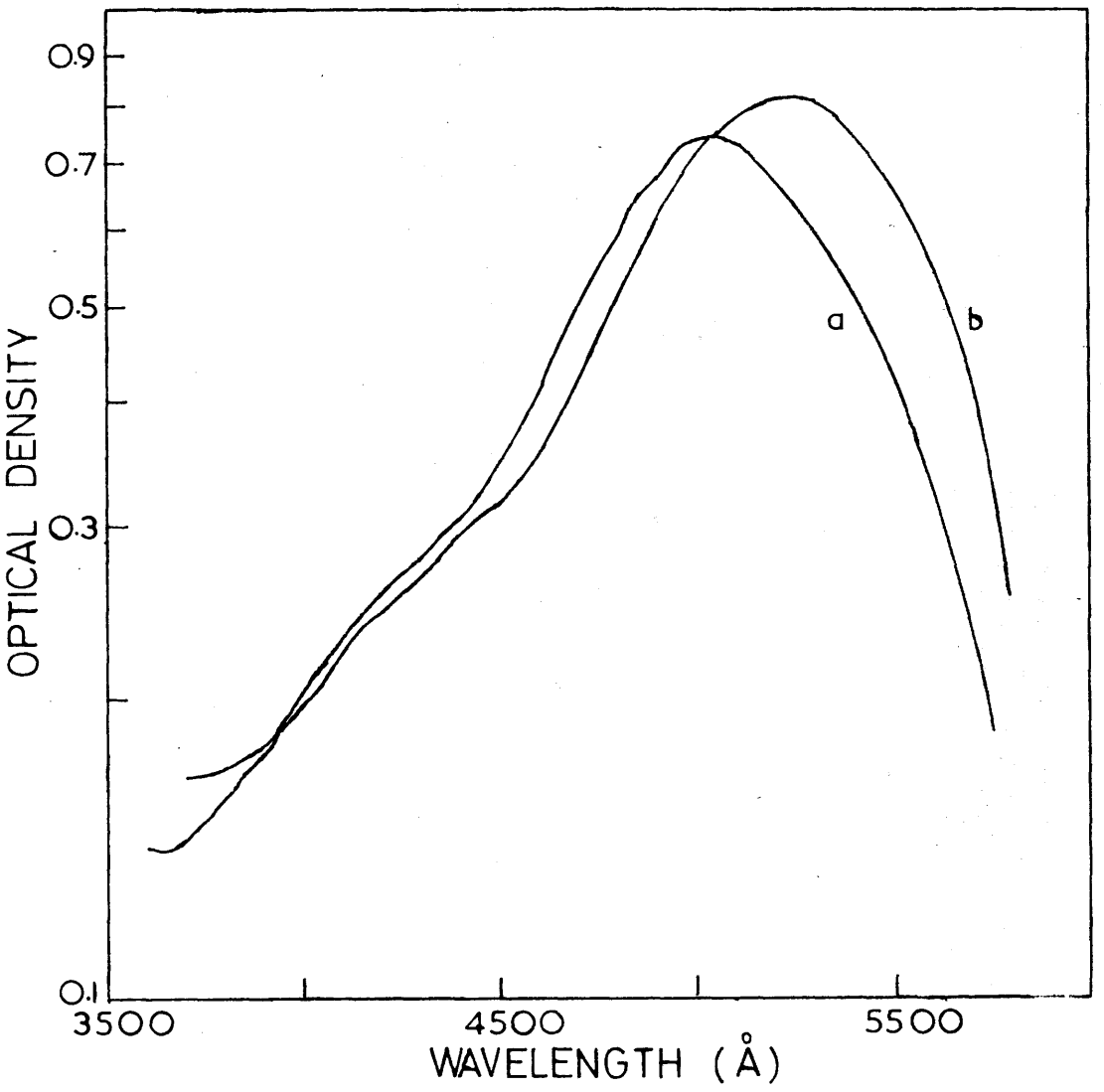


FIG.25. Spectral curves for dye II.

a: no solvent ; b: distilled benzyl alcohol.

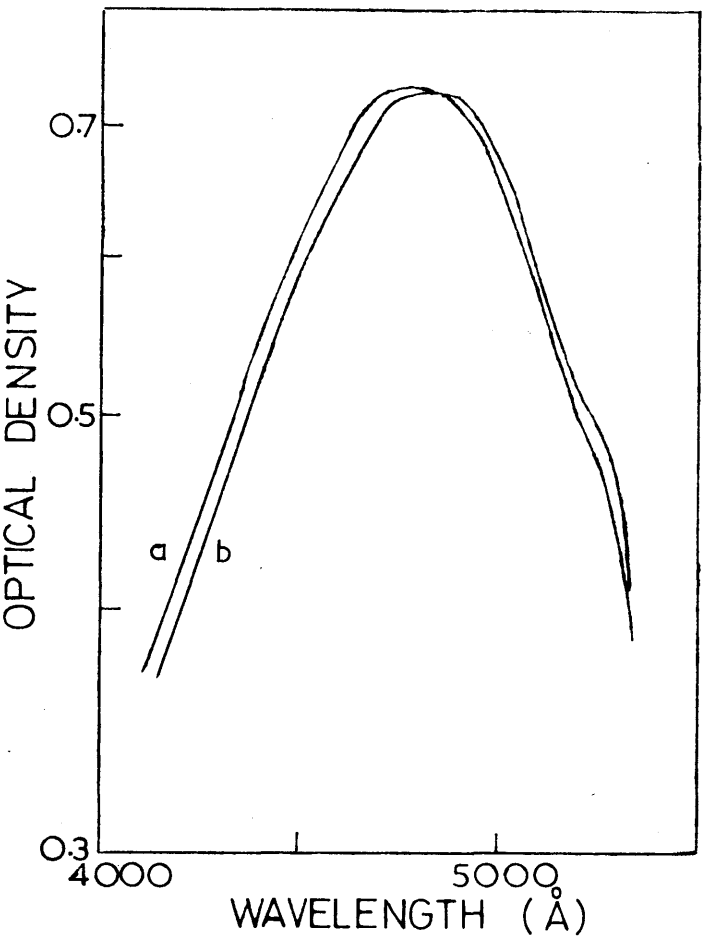


FIG.26. Spectral curves for dye VIII.

a: no solvent.

b: 3% (vol/vol) benzyl alcohol.

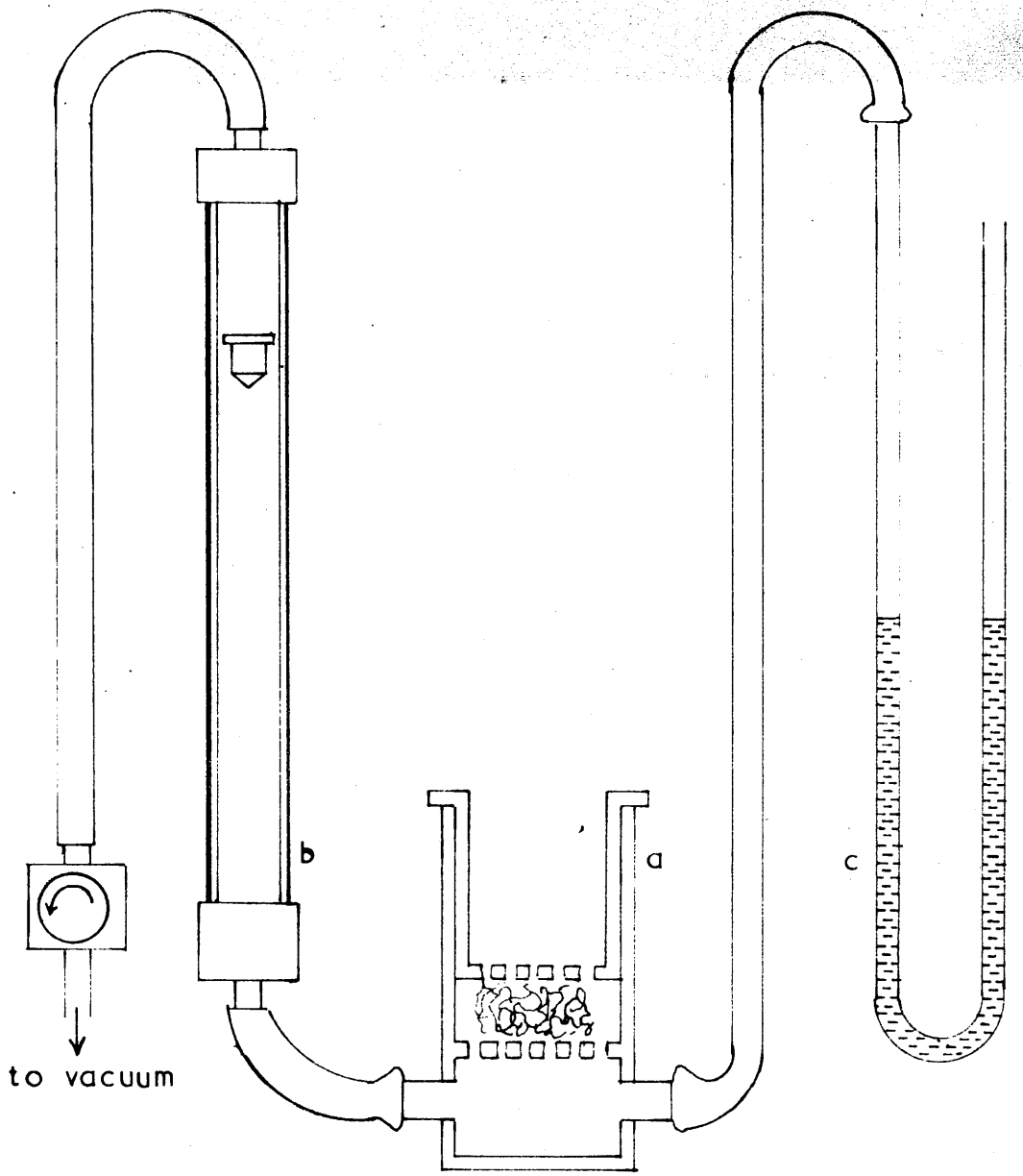


FIG.27. Air-permeability apparatus.

a: sample holder.

b: air-flow gauge.

c: manometer.

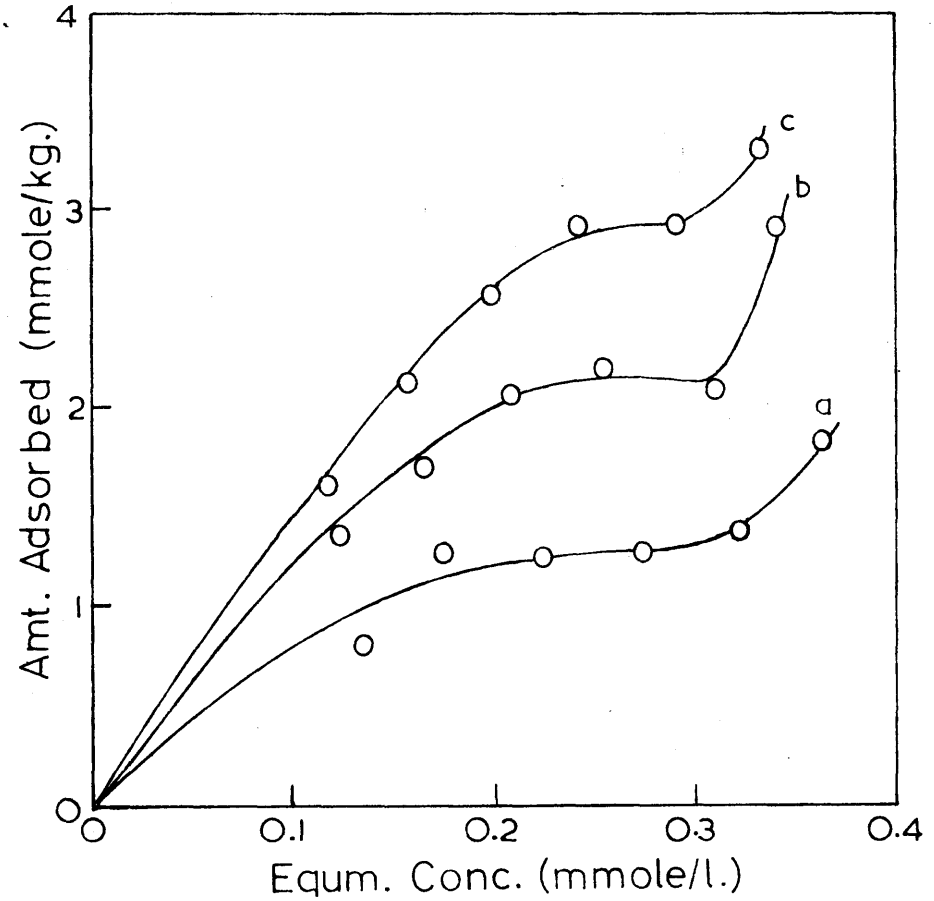


FIG.28. Typical short-period isotherms.

Adsorption isotherms of p-nitrophenol on nylon from xylene.

a: 30 min.

b: 60 min.

c: 90 min.

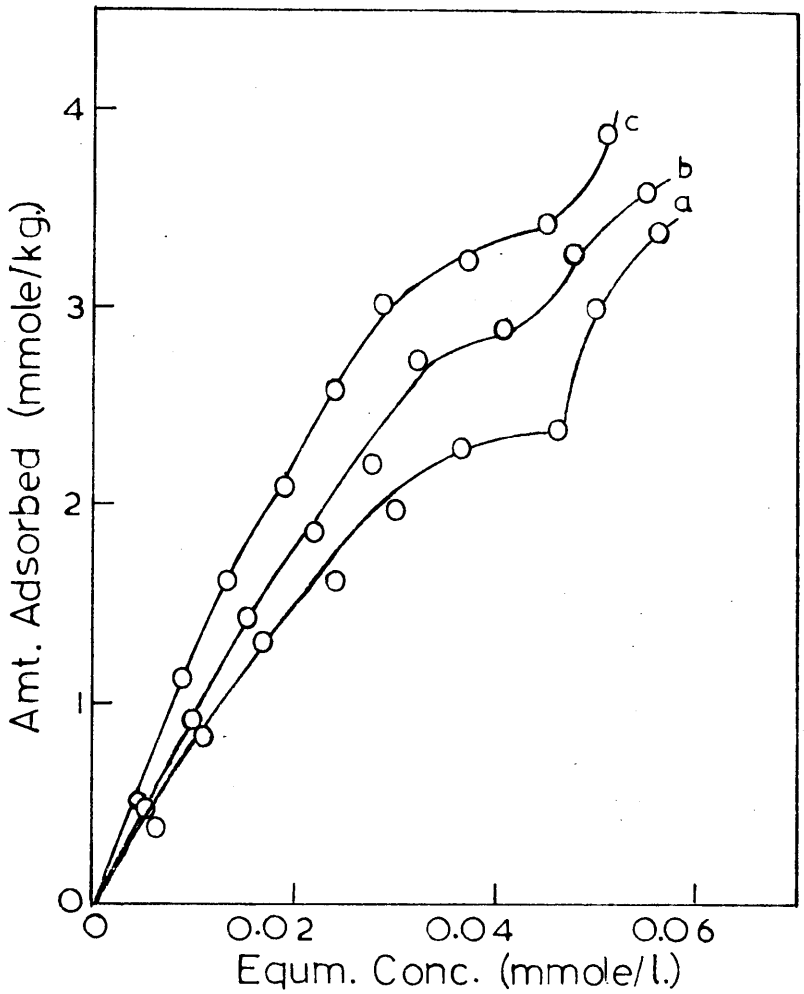


Fig.29. Typical short-period isotherms.

Adsorption isotherms of p-nitrophenol on nylon from cyclo-hexane.

a: 5 min.

b: 10 min.

c: 15 min.

LEGENDS TO FIG.30.

Short-period adsorption isotherm of p-nitrophenol on different substrates from n-hexane.

A:	Wool A	a: 30 min.;	b: 45 min.;	c: 60 min.
B:	Cuprammonium Rayon	a: 5 min.;	b: 15 min.;	c: 30 min.
C:	Terylene	a: 5 min.;	b: 10 min.;	c: 15 min.

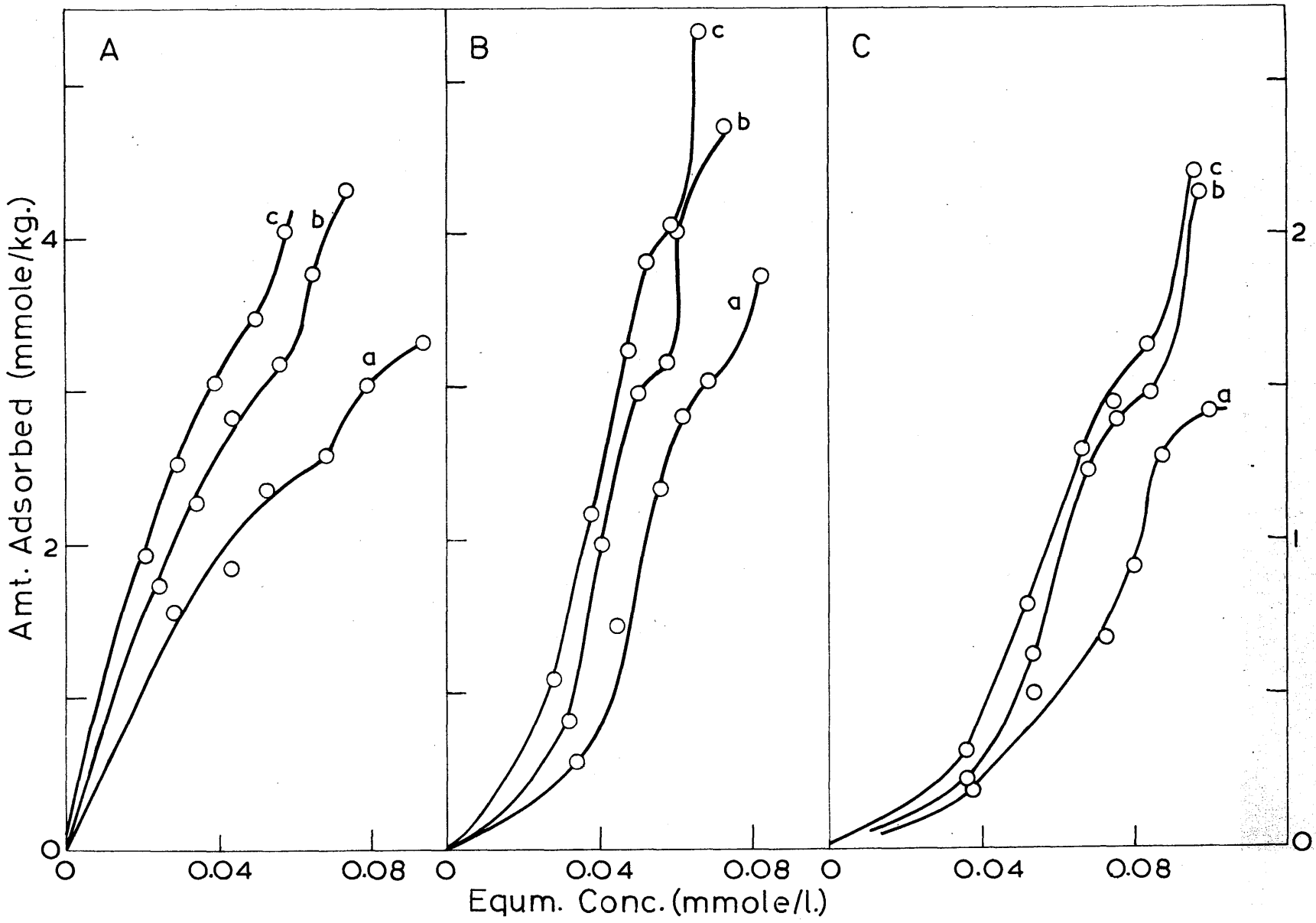


FIG.30.

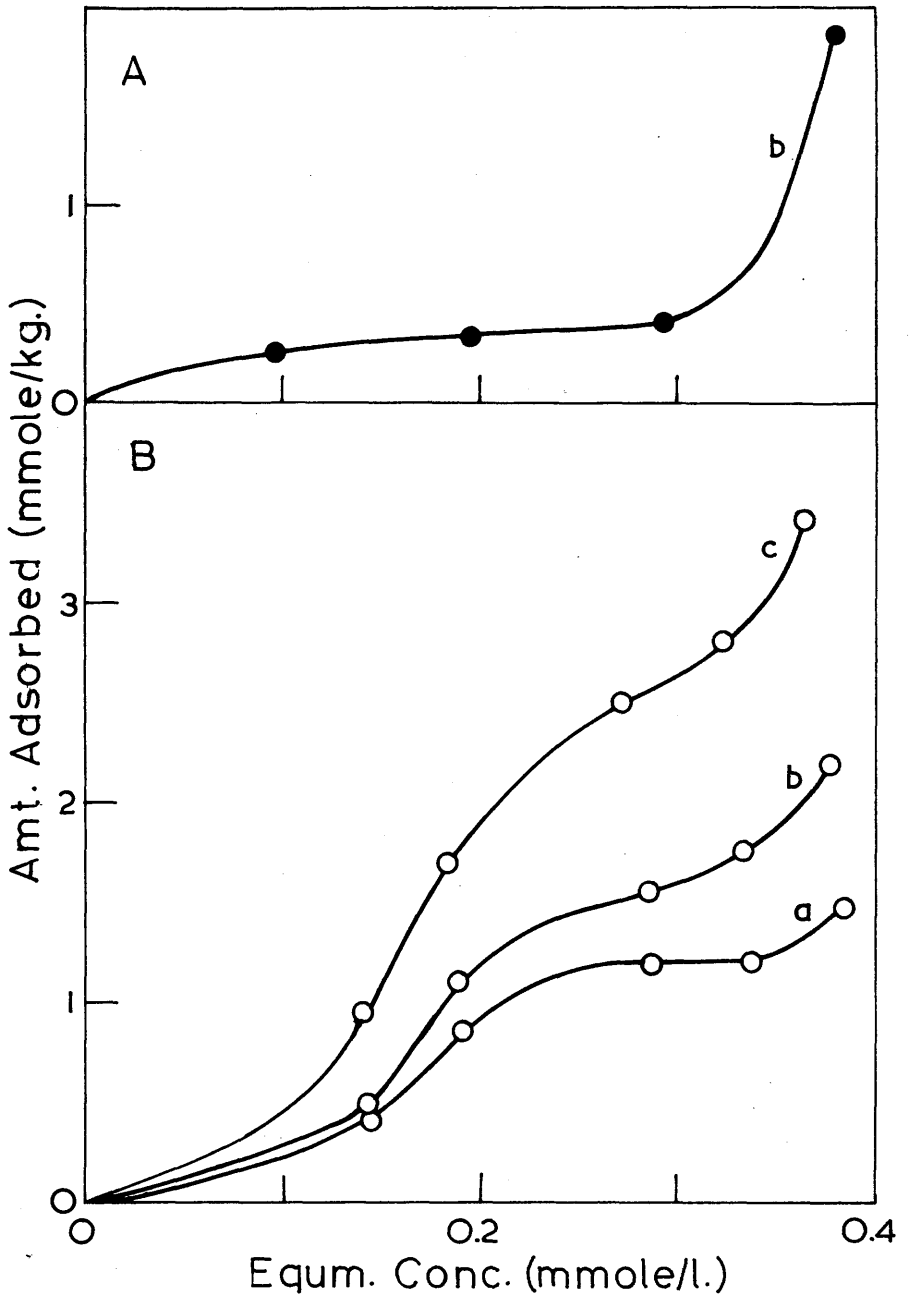


FIG.31. Short-period adsorption isotherm of phenol on nylon from n-heptane.

A: specially dry conditions.

B: normal condition.

a: 5 min.; b: 10 min.; c: 15 min.

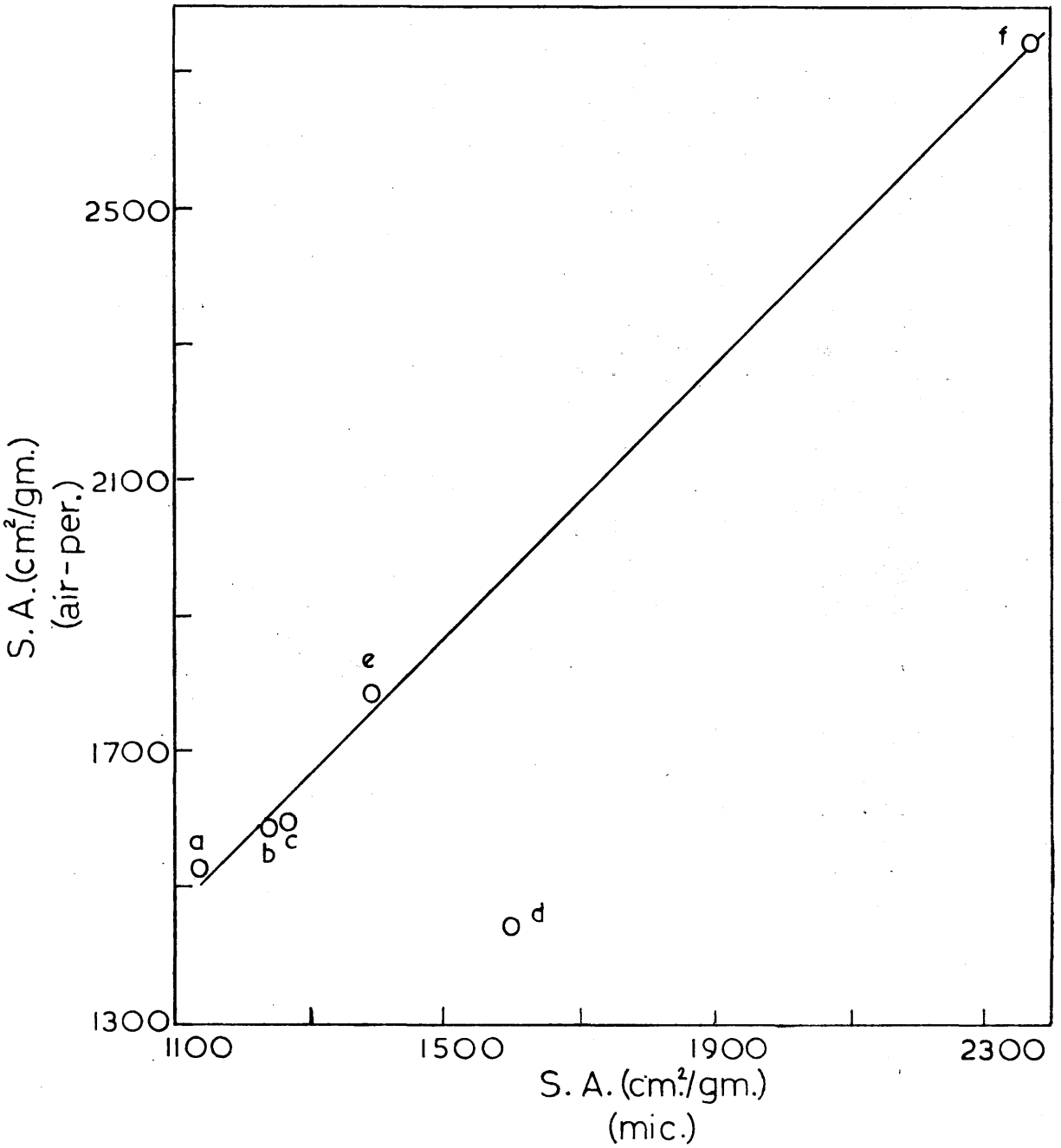


FIG.32. Relation between external surface area values by microscopic method and air-permeability method.

a: wool D; b: wool C; c: wool A, wool B;
d: nylon; e: Terylene; and f: cuprammonium rayon.

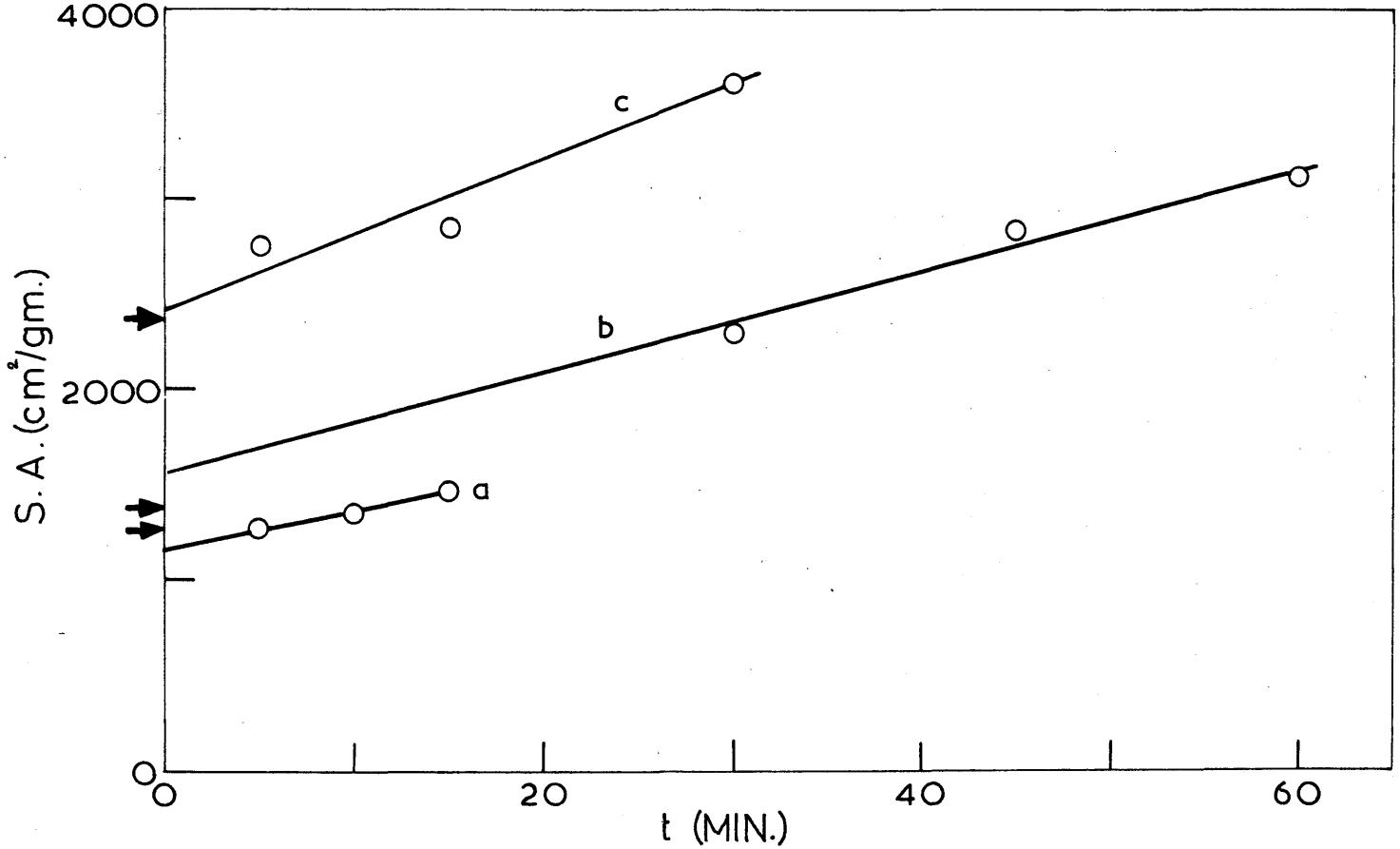


FIG.33. Relation between time and surface area at plateau of short-period isotherms (of Fig.30). The line extrapolated to zero time to obtain external surface area ($cm^2/gm.$) of fibre by adsorption method.

a: Terylene; b: wool A; cuprammonium rayon.

Arrows indicate surface area values by microscopic method.

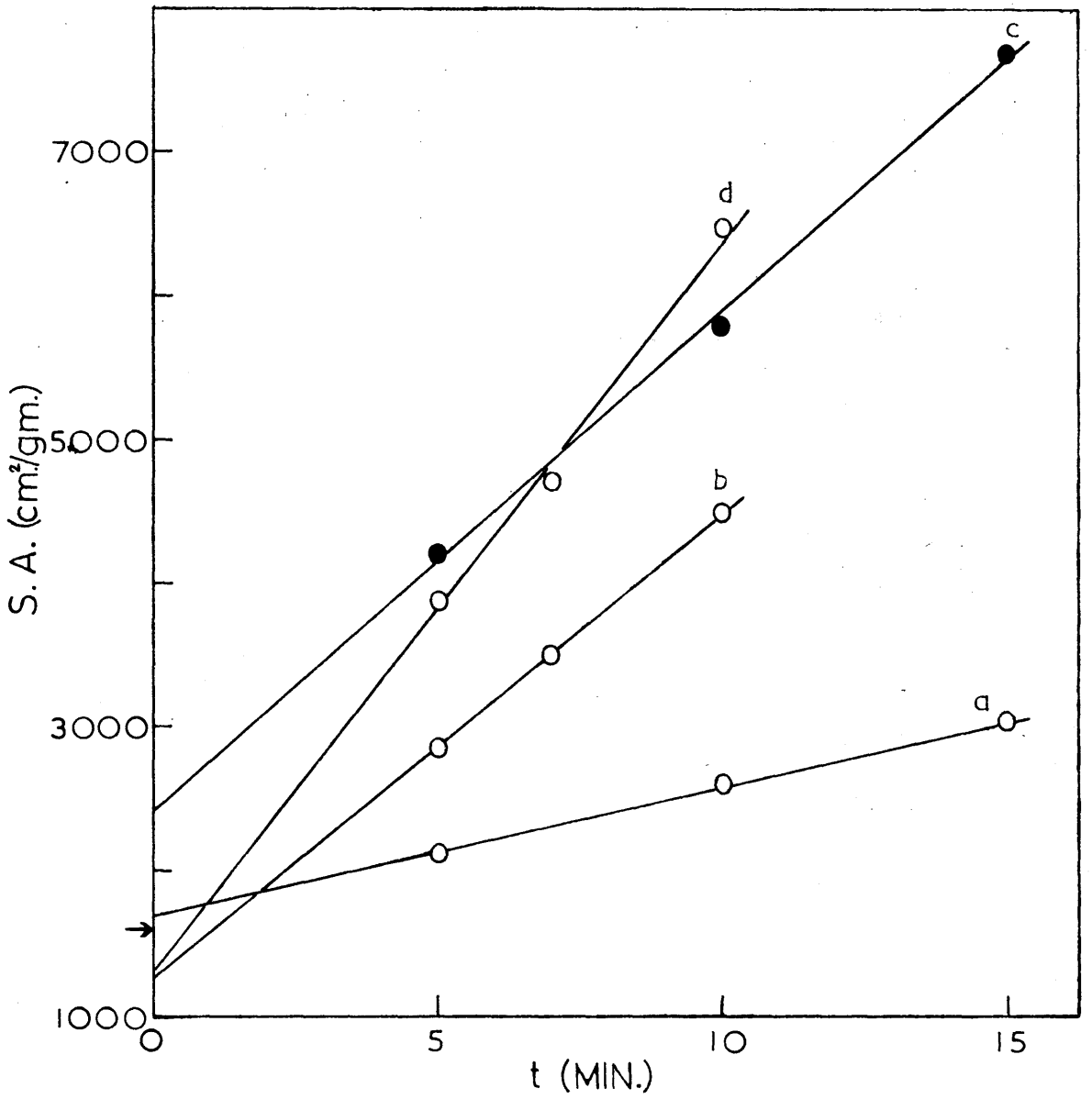


FIG.34. Relation between time and surface area at plateau of short-period isotherms of p-nitrophenol on nylon from different solvents.

a: cyclo-hexane; b: n-heptane; c: iso-octane; d: n-hexane
Arrow indicates the surface area value by microscopic method.
Solubility of p-nitrophenol in these solvents is low.

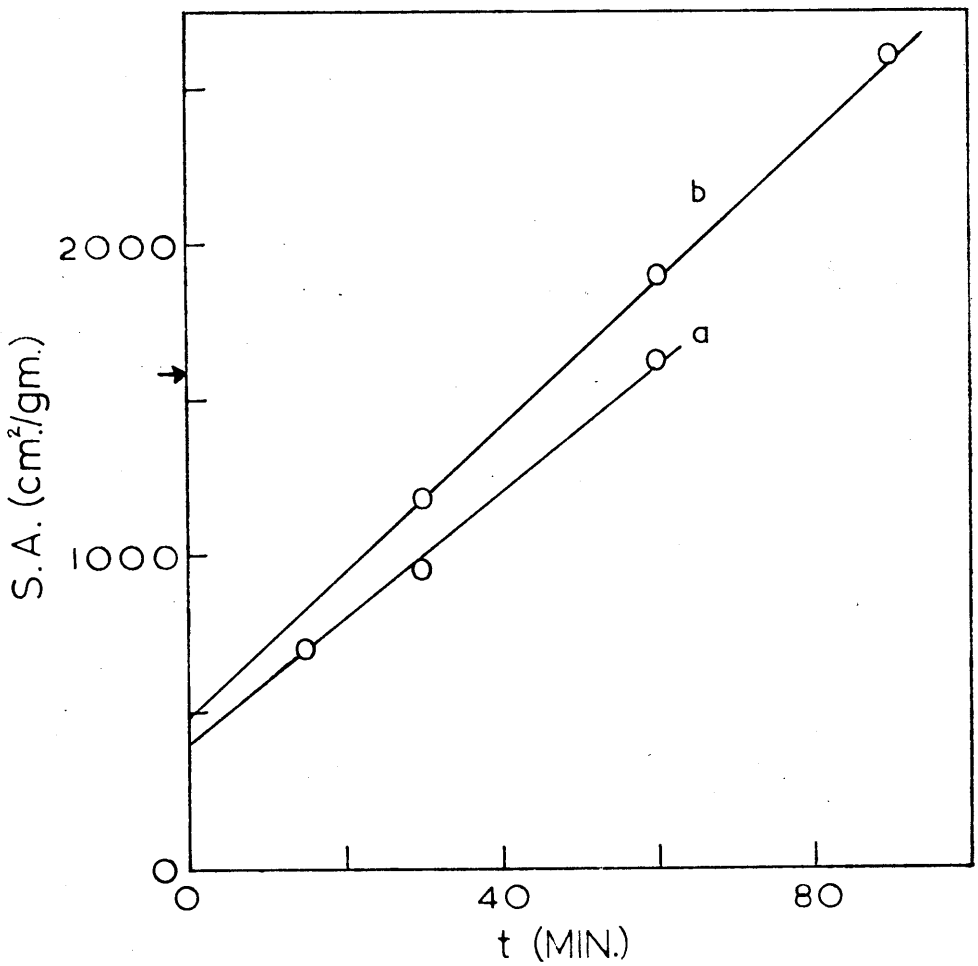


FIG.35. Relation between time and surface area at plateau of short-period isotherms of p-nitrophenol on nylon from different solvents.

a: Toluene ; b: Xylene.

Arrow indicates the surface area value by microscopic method.

Solubility of p-nitrophenol in these solvents is — fairly high.

LEGENDS TO FIG.36.

Relation between the (log) solubility of p-nitrophenol in different solvents and the (log) external surface area value by adsorption method, from these solvents.

a: iso-octane ; b: n-heptane ; c: n-hexane ;

d: cyclo-hexane; e: cyclo-hexane : xylene (70:30).

(Experimental evidence (e) doubtful)

f: xylene, and g: toluene.

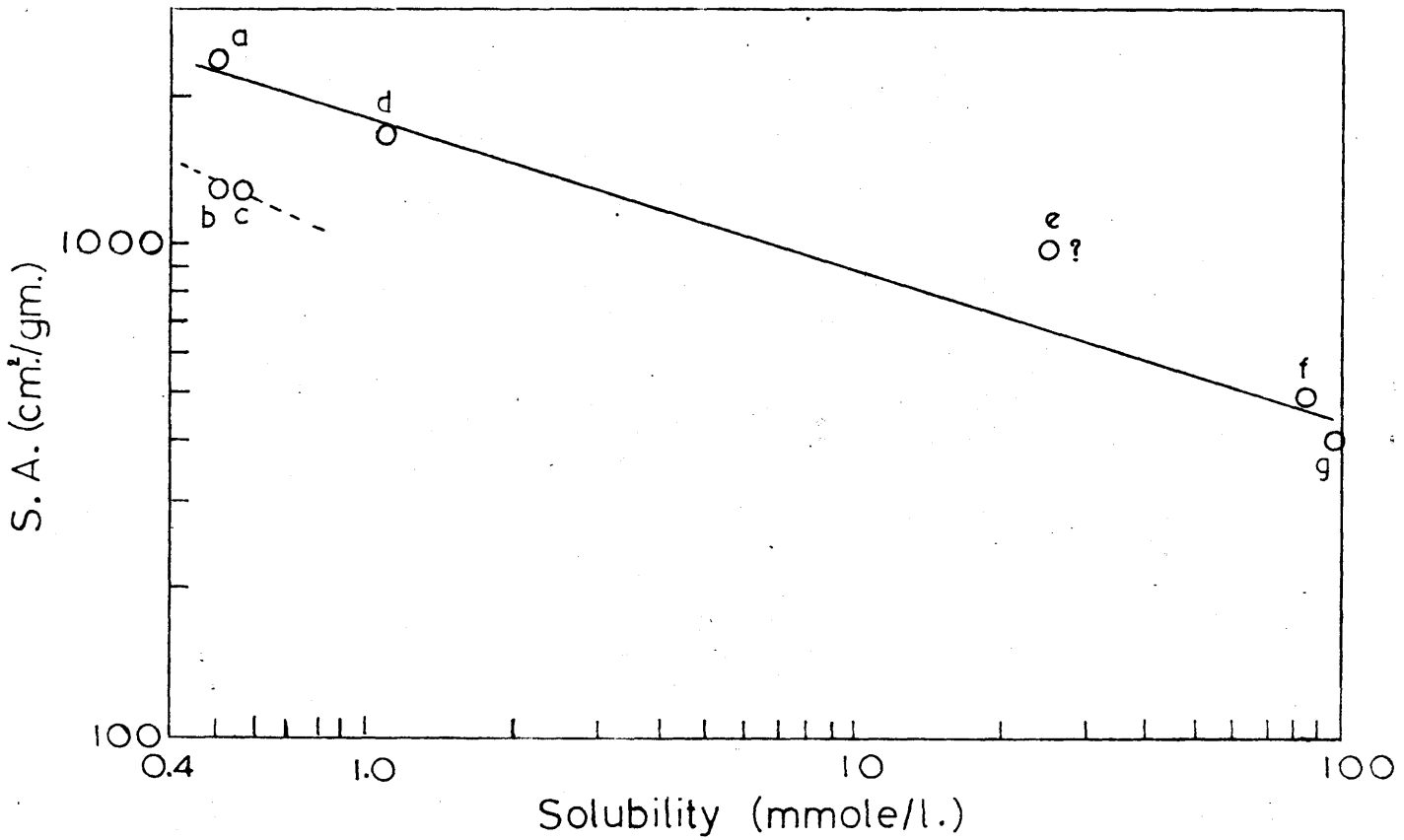


FIG. 36.

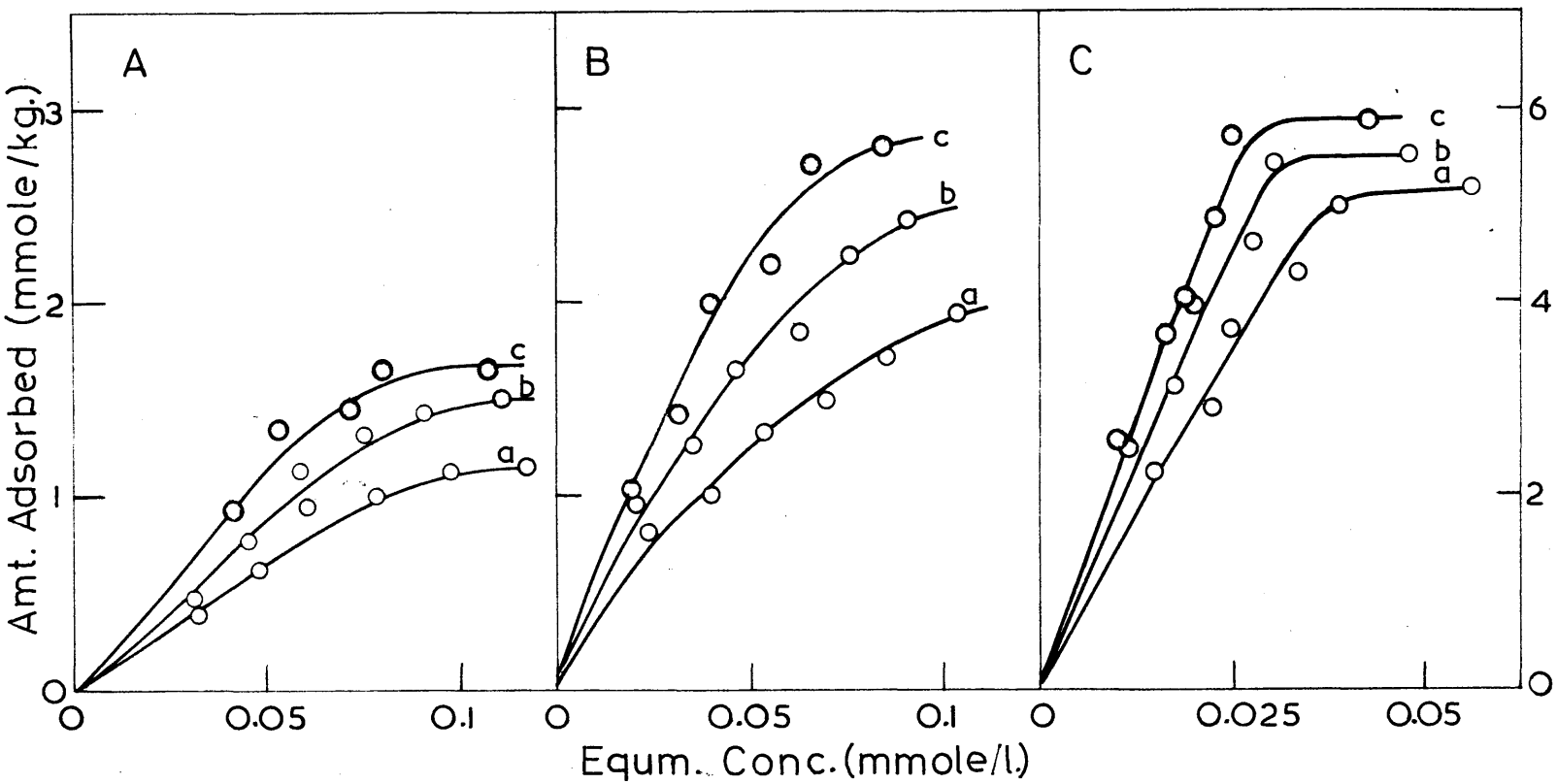


FIG.37. Short-period adsorption isotherms of p-nitrophenol on different wools from iso-octane.

A: wool A: a: 30 min.; b: 60 min.; c: 90 min.
B: wool D: a: 30 min.; b: 60 min.; c: 90 min.
C: wool B: a: 30 min.; b: 60 min.; c: 90 min.

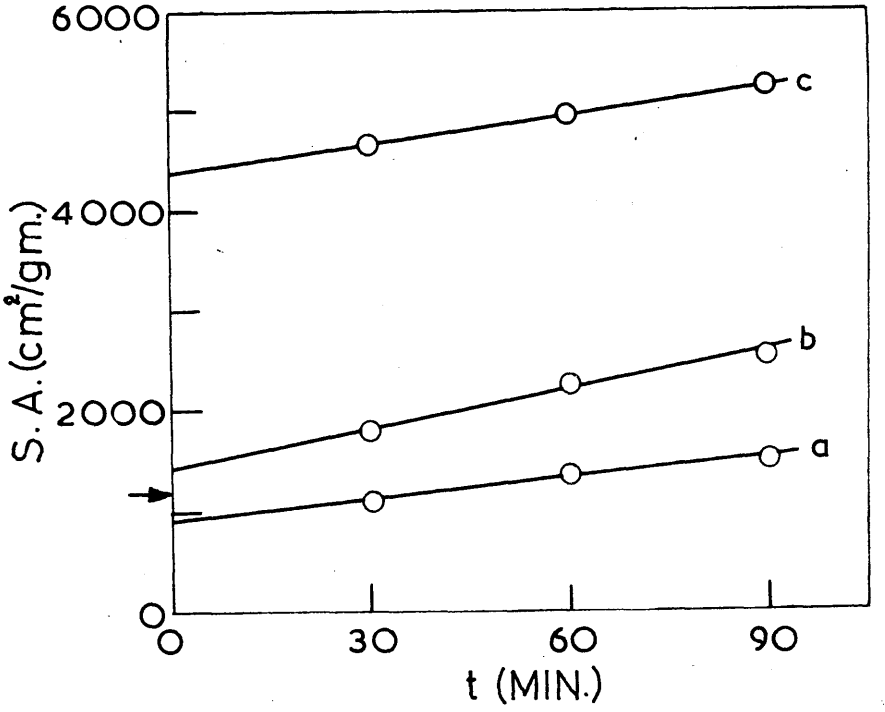


FIG.38. Relation between time and surface area at plateau of short-period isotherms (of Fig.37). The line extrapolated to zero time to obtain external surface area ($cm^2/gm.$) of fibre by adsorption method.

a: wool A ; b: wool D ; c: wool B.

Arrow indicates surface area value by microscopic method.

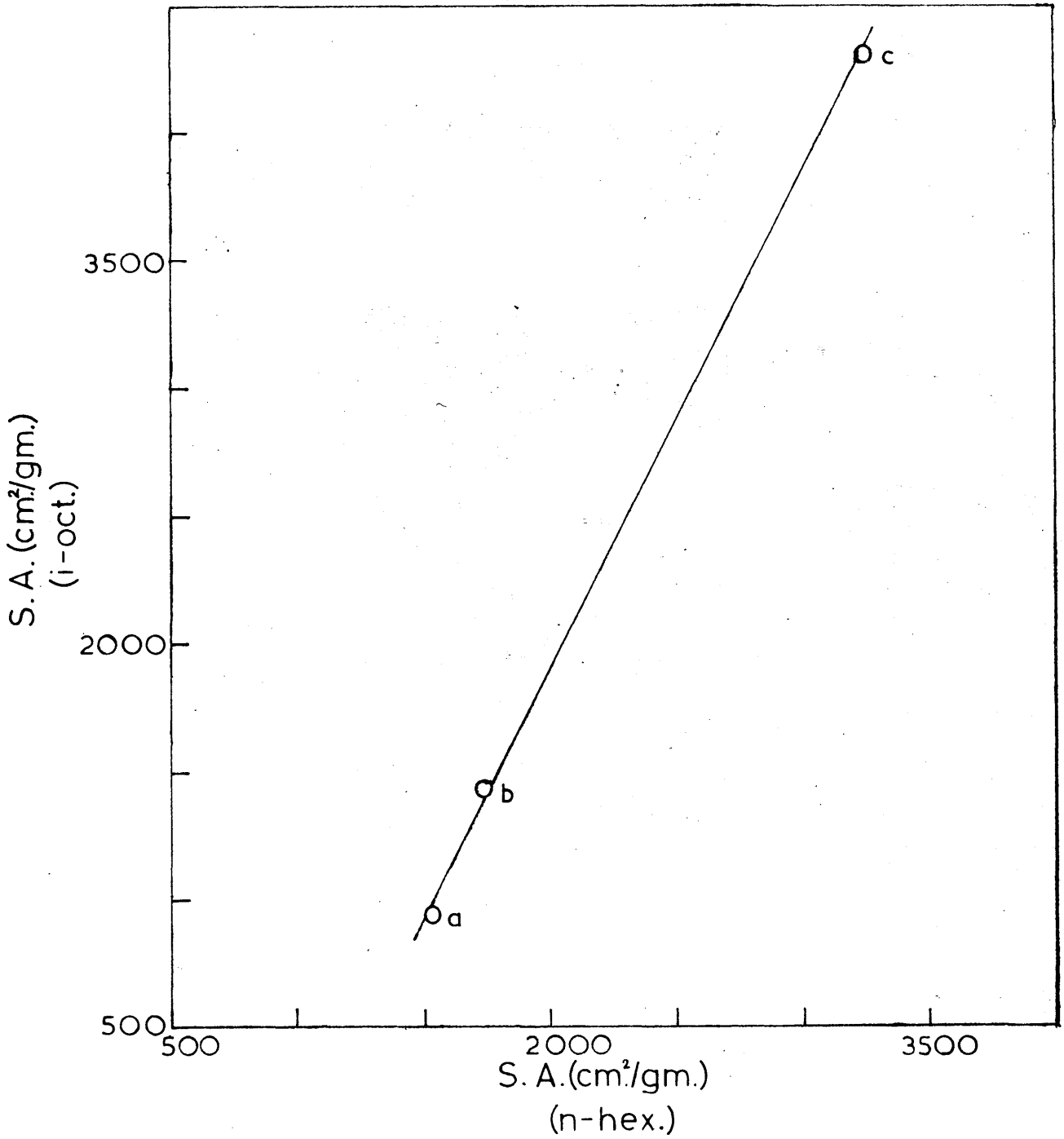


FIG.39. Relation between the surface area value, by adsorption method, of different wools from solvents n-hexane and iso-octane.

a: wool A ; b: wool D ; c: wool B.

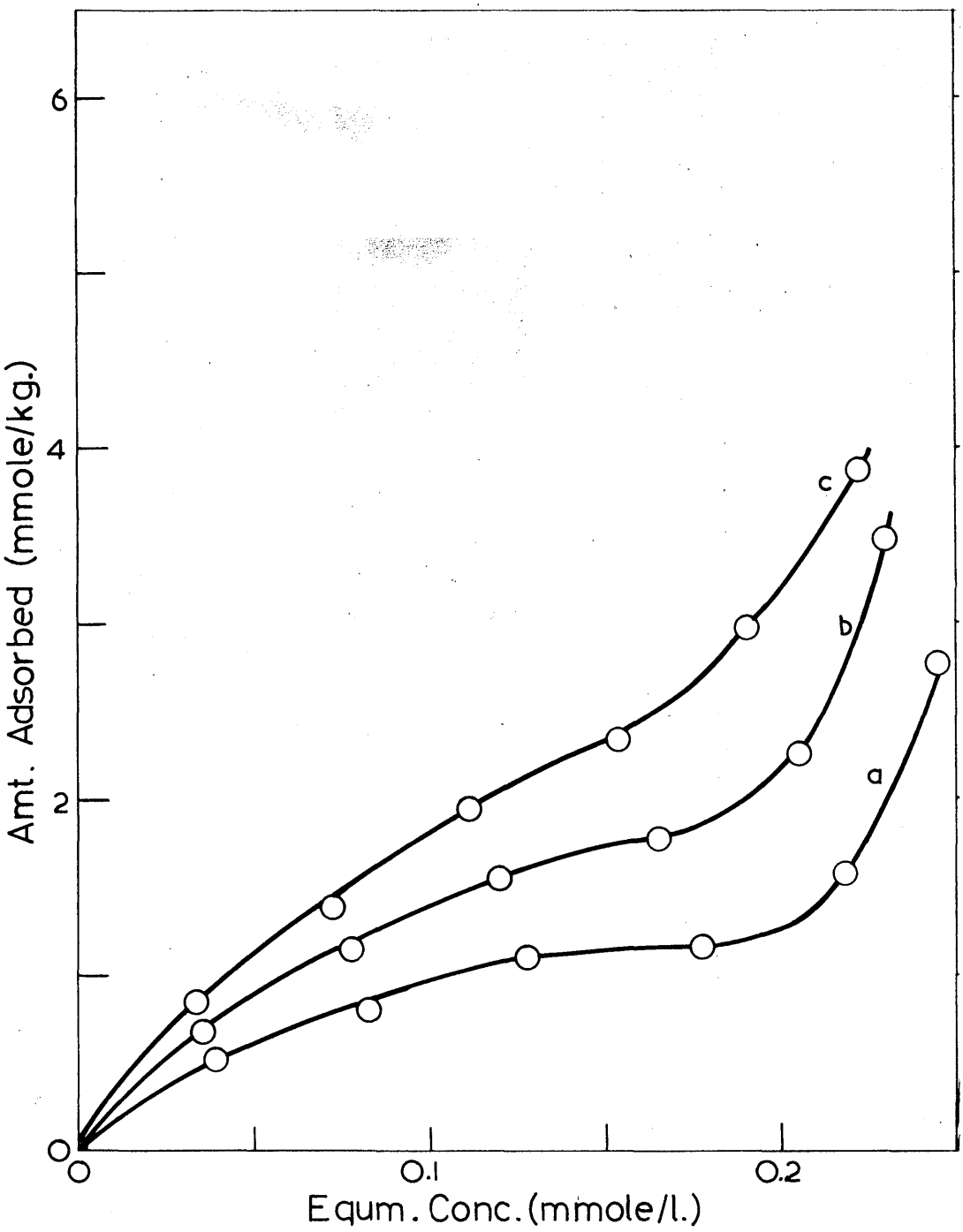


FIG.40. Short-period adsorption isotherms of Rhodamine B on wool A from water.

a: 30 min.; b: 60 min.; c: 90 min.

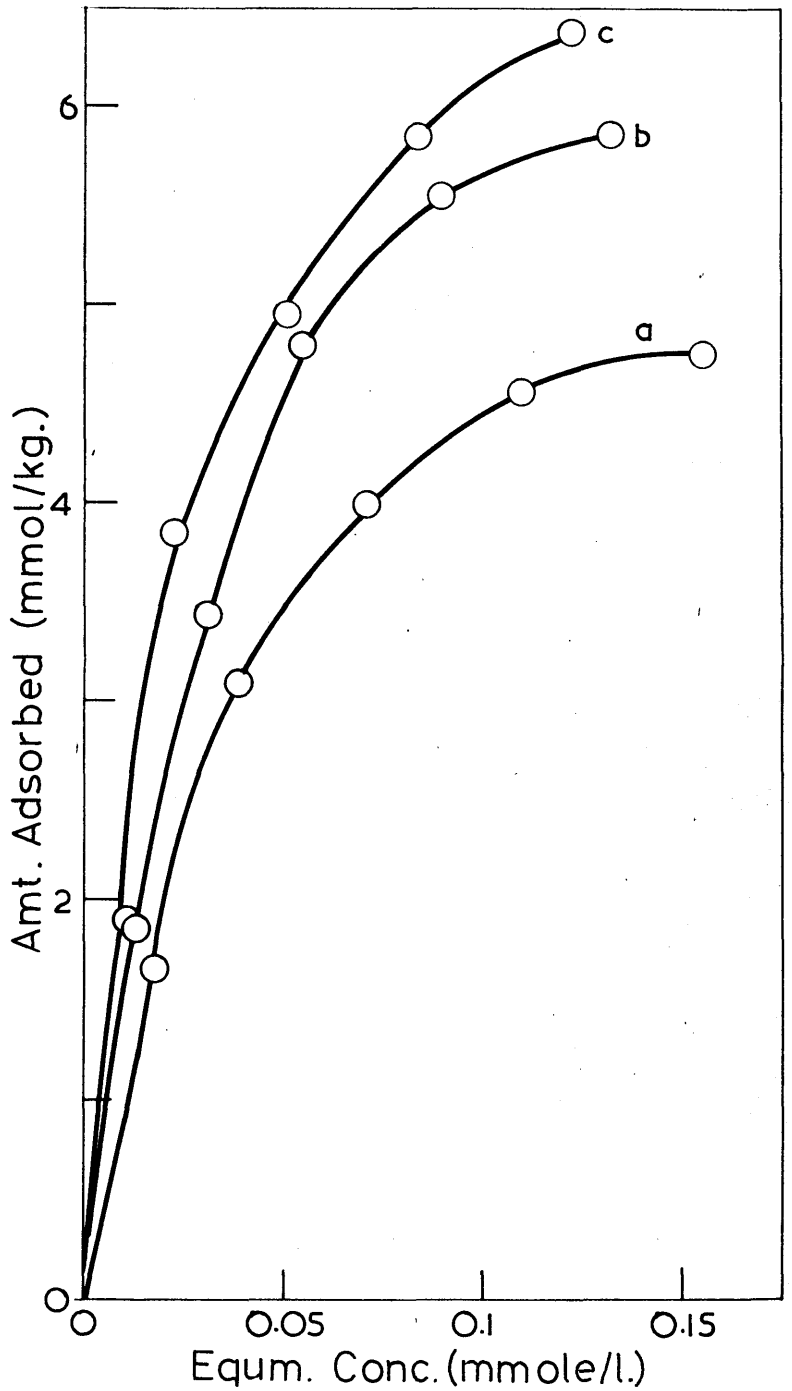


FIG.41. Short-period adsorption isotherm of Rhodamine 6 GB on wool A from water.

a: 15 min.; b: 30 min.; c: 45 min.

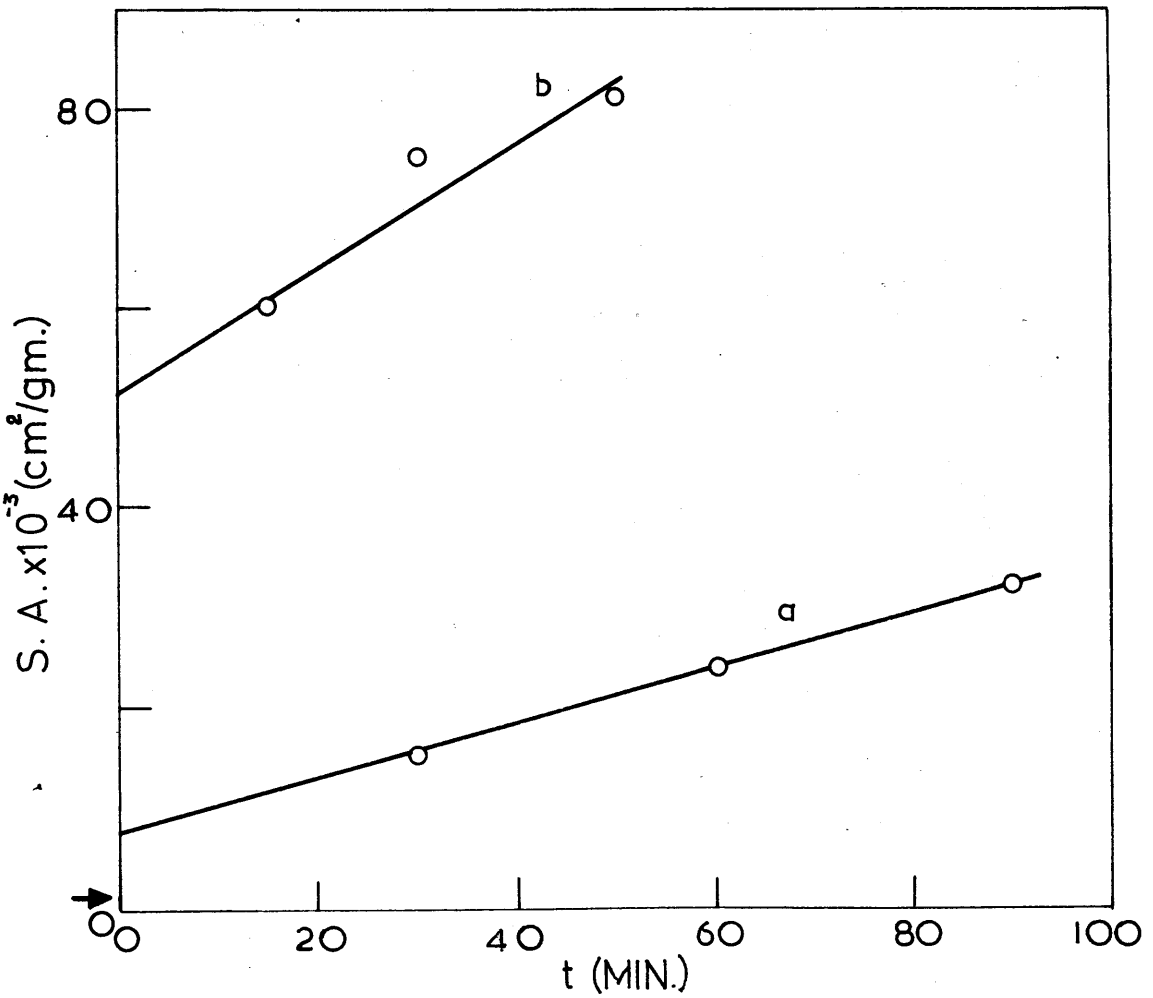


FIG.42. Relation between time and surface area at plateau of short-period isotherms (of Fig.40,41). The line extrapolated to zero time to obtain external surface area ($cm^2/gm.$) of fibre by adsorption method.

a: Rhodamine B ; b: Rhodamine 6 GB.

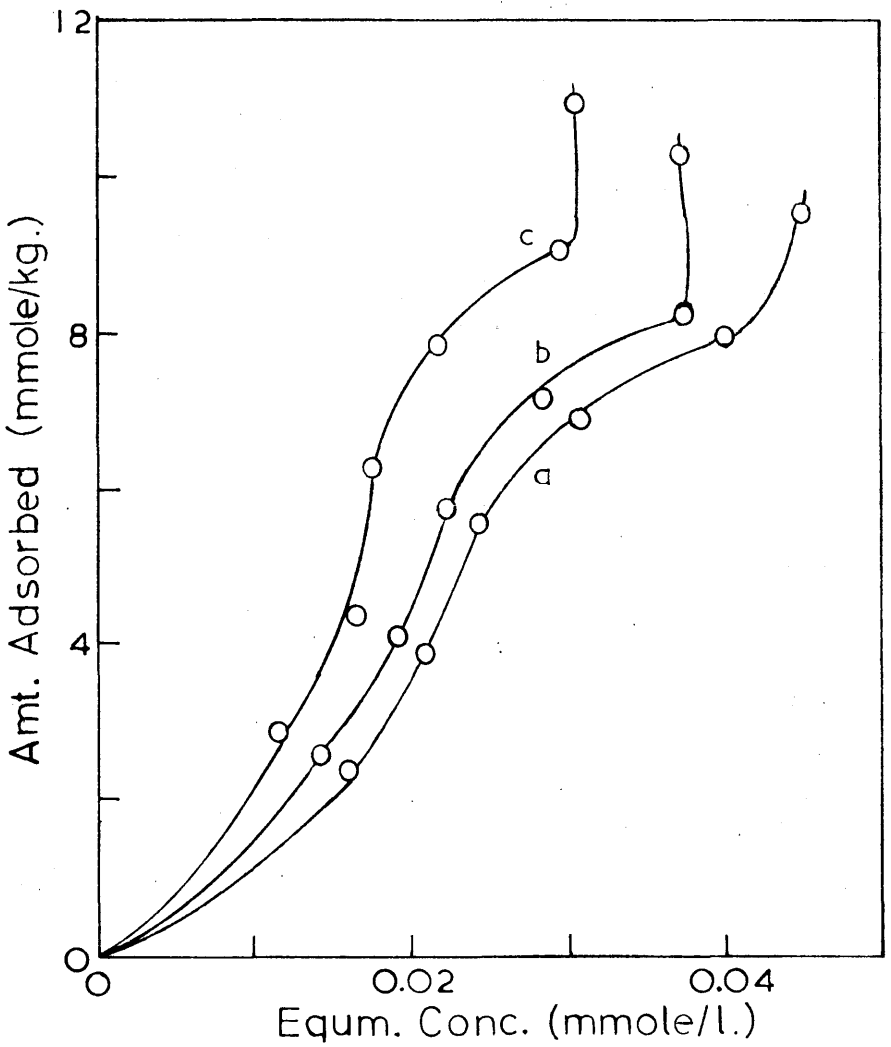


FIG.43. Short-period adsorption isotherms of p-nitrophenol on Paper 1 from iso-octane.

a: 5 min.; b: 15 min.; c: 30 min.

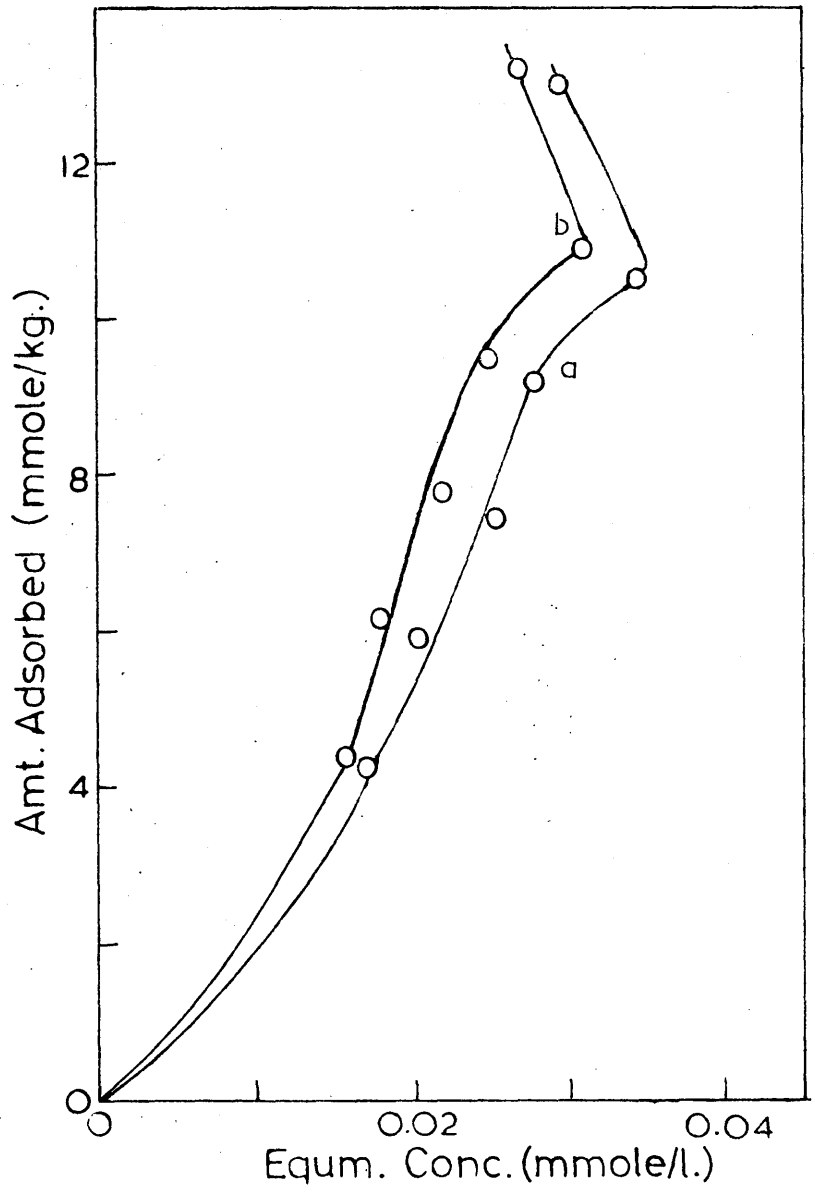


FIG.44. Short-period adsorption isotherms of p-nitrophenol on Paper 3 from iso-octane.

a: 15 min. ; b: 30 min.

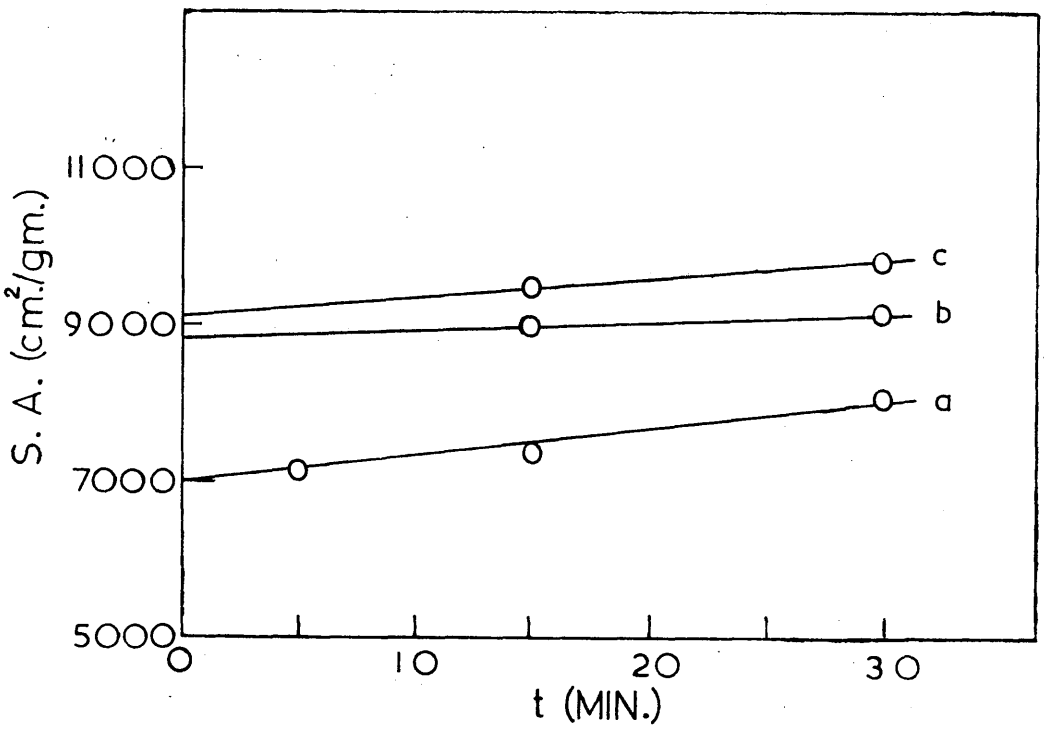


FIG.45. Relation between time and surface area at plateau of short-period isotherms of p-nitrophenol on Paper 1, 2 and 3 from Iso-octane.

a: Paper 1; b: Paper 2; c: Paper 3.

References

1. Gregg, "The Surface Chemistry of Solids", Chapman and Hall Ltd., London, 2nd Ed., 1961.
2. Glasstone, "Textbook of Physical Chemistry", Macmillan and Co. Ltd., London, 1955.
3. Adam, "The Physics and Chemistry of Surfaces", Oxford University Press, London, 3rd Ed., 1941.
4. Giles, Compte rendu du "XXVIIe Congres Internat. de Chemie Industrielle", Brussels, 1954.
5. Chipalkatti, Giles and Vallance, J.Chem. Soc., 1954, p.4375.
6. Allingham, Cullen, Giles, Jain and Woods, J. Appl. Chem., 1958, 8, 108.
7. Kipling, Proc of Second International Congress of Surface Activity, 1957, 3, 462.
8. Rattee, Research, 1959, 12, 15. (see also Vickerstaff, J. Soc. Dyers and Colourists, 1957, 73, 237).
9. Giles, Mehta, Stewart and Subramanian, J. Chem. Soc., 1954, p.4360.
10. Easton, Private Communication.
11. Schwab and Jockers, Naturwiss., 1937, 25, 44.
12. Fricke, Blaschke and Schmitt, Ber., 1938, 71, 1738.
13. Giles, Greczek and Nakhwa, J. Chem. Soc., 1961, p.93.
14. Brunauer, "Physical Adsorption of Gases and Vapours", Oxford University Press, 1942.

15. Giles and MacEwan, Proc of Second International Congress of Surface Activity, 1957, 3, 457.

16. Giles, MacEwan, Nakhwa and Smith, J. Chem. Soc., 1960, p.3973.

17. Giles and Nakhwa, J. Appl. Chem., 1962, 12, 266.

18. Easton, McKay and Patel, Unpublished.

19. Elder, Giles and Tolia, Unpublished.

20. McKay, Ph. D. Thesis, 1962, Glasgow University.

21. Sheppard and Newsome, J. Phys. Chem., 1929, 33, 1826.

22. Bull, J. Amer. Chem. Soc., 1944, 66, 1499.

23. Hailwood and Horrobin, Disc. Faraday Soc., 1948, 428, 84.

24. Speakman, J. Soc. Chem. Ind., 1930, 49, T209.

25. Trotman, J. Soc. Dyers and Colourists, 1928, 44, 49.

26. Larose, J. Soc. Dyers and Colourists, 1954, 70, 77.

27. McLaren and Rowen, J. Poly. Sci., 1951, 7, 289.

28. Carlene, J. Soc. Dyers and Colourists, 1944, 60, 232.

29. Pierce, J. Textile Inst., 1929, 21, T133.

30. Cassie, Trans. Faraday Soc., 1945, 41, 450, 458.

31. Gilbert, Symposium on Fibrous Proteins, S.D.C., Bradford, 1946, p.96.

32. Kanamaru and Chao, Kolloid Z., 1938, 84, 85.

33. Lauter, Kolloid Z., 1944, 107, 86.

34. King, Trans. Faraday Soc., 1945, 41, 325.

35. Chipalkatti, Chipalkatti and Giles, J. Soc. Dyers and Colourists, 1955, 71, 652.

36. Astbury and Dawson, J. Soc. Dyers and Colourists, 1938, 54, 6.

37. McBain and Bakr, J. Amer. Chem. Soc., 1926, 48, 690.

38. Chipalkatti and Giles, Nature, 1950, 165, 735.

39. Speakman, J. Soc. Dyers and Colourists, 1933, 49, 180.

40. King, Trans. Faraday Soc., 1947, 43, 552.

41. King, J. Soc. Dyers and Colourists, 1950, 66, 27.

42. Quynn, Textile Res. J., 1963, 33, 21.

43. Boyd, Adamson and Myers, J. Amer. Chem. Soc., 1947, 69, 2836.

44. Kunin and Myers, J. Phys. Chem., 1947, 51, 1111.

45. Vickerstaff, J. Soc. Dyers and Colourists, 1953, 69, 279.

46. Valko, J. Soc. Dyers and Colourists, 1939, 55, 173.

47. Vickerstaff, "The Physical Chemistry of Dyeing", Oliver and Boyd Ltd., Edinburgh and London, 2nd Ed., 1954.

48. Crank, "Mathematics of Diffusion", Clarendon Press, Oxford, 1956.

49. Sumner, J. Royal Inst. Chem., 1960, 84, 389.

50. Speakman and Smith, J. Soc. Dyers and Colourists, 1936, 52, 121.

51. Wilson, Phil. Mag., 1948, 39, 48.

52. Crank, Phil. Mag., 1948, 39, 140.

53. Crank, Phil. Mag., 1948, 39, 362.

54. Alexander and Hudson, Textile Res. J., 1950, 20, 481.

55. Morton, Textil-Rund., 1949, 4, 39.

56. Royer, Fiddle and Millson, Amer. Dyestuff Reptr., 1948, 37, 116.

57. Morton, Symposium on Fibrous Proteins, S.D.C., Bradford, 1946, p.155.

58. Peters and Speakman, J. Soc. Dyers and Colourists, 1949, 65, 63.

59. Proctor and Wilson, J. Chem. Soc., 1916, p.307.

60. Neale, Trans. Faraday Soc., 1949, 45, 1027.

61. Booth, Trans. Faraday Soc., 1948, 44, 796.

62. Sheppard, Houck and Dittmar, J. Phys. Chem., 1942, 46, 158.

63. Peters and Lister, Disc. Faraday Soc., 1954, 16, 24.

64. Millson, Amer. Dyestuff Reptr., 1955, 44, 417.

65. Gralen, Lindberg and Phillip, Nature, 1948, 162, 458.

66. Lindberg, Textile Res. J., 1950, 20, 381.

67. Lemin and Vickerstaff, Symposium on Fibrous Proteins, S.D.C., Bradford, 1946, p.129.

68. Meggy, J. Soc. Dyers and Colourists, 1950, 66, 510.

69. Alexander and Charman, Textile Res. J., 1950, 20, 761.

70. Townend, J. Soc. Dyers and Colourists, 1945, 61, 144.

71. Townend and Simpson, J. Soc. Dyers and Colourists, 1946, 62, 47.

72. Nicholls, J. Soc. Dyers and Colourists, 1956, 72, 479.

73. Peters and Stevens, J. Soc. Dyers and Colourists, 1956, 72, 100, and Dyer, 1956, 115, 327.

74. Lister, Textil-Rund., 1956, 11, 463.

75. Delmenico, Textile Res. J., 1957, 27, 899.

76. Beal, Dickinson and Bellhouse, J. Soc. Dyers and Colourists, 1960, 76, 333.

77. Karrholm, J. Textile Inst., 1960, 51, T1323.

78. Karrholm and Lindberg, Textile Res. J., 1956, 26, 528.

79. Peters, Stevens, Budding, Burdett and Sykes, J. Soc. Dyers and Colourists, 1960, 76, 543.

80. Hadfield and Lemin, J. Textile Inst., 1960, 51, T1351.

81. Medley and Ramsden, J. Textile Inst., 1960, 51, T1311.

82. Siegrist and Hobday, Milliand Textilber., 1960, 41, 1119.

83. Alexander and Stacey, J. Soc. Dyers and Colourists, 1956, 72, 241.

84. A.A.T.C.C., Delaware Valley Section, Amer. Dyestuff Reptr., 1958, 47, 789.

85. Cassie, J. Soc. Dyers and Colourists, 1960, 76, 617.

86. Medley and Andrews, Textile Res. J., 1960, 30, 855.

87. Aickin, J. Soc. Dyers and Colourists, 1944, 60, 60.

88. Montgomary, B.Sc. Thesis, R.C.S.T., 1960.

89. Dandekar and Giles, Chem and Ind., 1963, p.289.

90. Gilbert, Proc. Royal Soc., 1944, 183A, 167.

91. Lemin, quoted by Vickerstaff, of Ref. 45.

92. Glenz, Beckman and Wunder, J. Soc. Dyers and Colourists, 1959, 75, 141.

93. Sekido, Tokyo Institute of Technology, private communication.

94. Odajima, J. Soc. Dyers and Colourists, 1959, 75, 255.

95. Bruce, Giles and Jain, J. Chem. Soc., 1958, p.1610.

96. Cameron, Giles and MacEwan, J. Chem. Soc., 1958, p.1224.

97. Wright, Disc. Faraday Soc., 1954, 16, 58.

98. Hudson, Disc. Faraday Soc., 1954, 16, 14.

99. Giles and MacEwan, J. Chem. Soc., 1959, p.1791.

100. Giles and McKay, Unpublished.

101. Arshid, Giles and Jain, J. Chem. Soc., 1956, p.559.

102. Lewis and Calvin, Chem. Rev., 1939, 25, 273.

103. Lewis, J. Amer. Chem. Soc., 1945, 67, 770.

104. Lemin and Vickerstaff, Trans Faraday Soc., 1947, 43, 491.

105. Campbell and Giles, J. Soc. Dyers and Colourists, 1958, 74, 164.

106. Giles, Rahman and Smith, J. Chem. Soc., 1961, p.1209.

107. El-Mariah and Nursten, J. Soc. Leather Trades' Chemists, 1963, 47, 131.

108. Rowen and Blaine, Ind. Eng. Chem., 1947, 39, 1659.

109. Nakhwa, Ph. D. Thesis, 1961, Glasgow University.

110. Paneth and Thimann, Ber., 1924, 57B, 1215.

111. Orr, Blacker and Craig, J. Inst. Metals, 1952, 4, 1, 657.

112. Kozeny, Ber. Wien Akad., 1927, 136A, 271.

113. Lord, J. Textile Inst., 1955, 46, T191 and 1956, 47, T209.

114. Anderson, J. Textile Inst., 1954, 45, P312.

115. Peirce and Lord, J. Textile Inst., 1939, 30, T173.

116. Clark, Paper Trade J., 1942, 115, 32.

117. Kenrick, J. Amer. Chem. Soc., 1940, 62, 2838.

118. Bartell and Fu, Colloid Symposium Monograph, 1930, 7, 138.

119. Bowden and Rideal, Proc. Royal Soc., 1928, A120, 59, 80.

120. Constable, Nature, 1926, 118, 730; Proc. Royal Soc., 1928, A119, 196, 202.

121. Paneth and Vorwerk, Z. Phys. Chem., 1922, 101, 445.

122. Braggs, J. Phys. Chem., 1913, 22, 216.

123. Clunie and Giles, Chem. and Ind., 1957, p.481.

124. Harkins and Gans, J. Amer. Chem. Soc., 1931, 53, 2804.

125. Hirst and Lankester, Trans. Faraday Soc., 1951, 47, 315.

126. Emersleben, Physik Z., 1925, 26, 601.

127. Sullivan, J. Appl. Phys., 1940, 11, 761.

128. Beamesderfer, Thode, Chase and Hubbard, Tappi, 1952, 35, 374.

129. Gasser and Kipling, Proc. of Fourth Conf. on Carbon, 1960, p.55.

130. Casey, "Pulp and Paper, Chemistry and Chemical Technology", Interscience Publishers Inc., Newyork, 2nd Ed., Vol 2, 1960.

131. Ingmanson and Andrews, Tappi, 1959, 42, 29.

132. Clyde Paper Co., Glasgow, private communication.